Evaluation of corrosion inhibitor simulating conditions of operation

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Abstract. Operating conditions at the head of oil wells are critical, in addition to injecting water to increase the pressure while maintaining production cause deterioration in the metallic structures that transport fluids. One way to maintain integrity is the injection of inhibitors which plays an important role in protecting the pipes. In this study a molecule N-PHENYL NITRONE was obtained, which was evaluated by electrochemical tests (LPR) and Tafel Polarization Curves in a reactor controlling environments containing different dosages, pressure values, temperatures and flow velocity using working electrodes tubing API N 80, the reactor was connected to a potentiostat to determine corrosion rates, allowing the analysis of the influence of each variable on the protective behaviour of the inhibitor, and its efficiency against the decrease of the deterioration of the pipes. Corrosion products are analysed by X-Ray Diffraction (XRD). Photographic records of the surface verify the formation of iron carbonate (FeCO₃). In addition, a mathematical analysis of the independent variables is performed to evaluate the effect that it has on the efficiency of corrosion inhibition.

1. Introduction
The analysis of residual corrosion inhibitor concentration in production waters has been used for years to monitor the corrosion protection of oilfield systems. [1] A corrosion inhibitor is a material that fixes or covers the metal surface, providing a protective film that stops the corrosive reaction [2]. The corrosion inhibitors are added in small concentrations to the corrosive medium, acting at the metal-solution interface, significantly reducing the corrosion rate of the metal material, exposed to it [3]. Corrosion inhibitors generally control corrosion by forming thin films that modify the medium on the metal surface [4]. The use of corrosion inhibitors is one of the most common methods to control corrosion [5], due to their excellent performance in "sweet" and "acid" environment.

Dry CO₂ gas is not itself corrosive at the temperatures encountered within oil and gas production systems but is so when dissolved in an aqueous phase through which it can promote an electrochemical reaction between steel and the contacting aqueous phase. CO₂ will mix with the water, forming carbonic acid making the fluid acidic [6,7] and is by far the most prevalent form of attack encountered in oil and gas production [8].

These inhibitors are mainly constituted of organic nitrogen compounds, being the most common, which have as part of their structure long chains of hydrocarbons (usually C18). Today these inhibitors are constituted by long aliphatic chains (diamine) or long carbon chains (imidazolines) [9]. Polymers are widely used as effective corrosion inhibitors [10]. Corrosion inhibition by these organic compounds is mostly attributed to their adsorption ability on metal surface and the subsequent formation of a protective layer, which can block the active sites on metal surface and thereby suppress
The corrosion attack [11]. The adsorption process of organic molecules on metal surface depends mainly on the surface charge of metal, the chemical structure of organic molecule and the type of aggression medium [12].

2. Experimental procedure
Figure 1 shows the reactor used to perform the tests, showing the parts of the system, it is connected to a potentiostat to perform electrochemical tests at the moment of obtaining the values of each of the variables at work.

![Figure 1. Autoclave for measurement of corrosion kinetics, high pressure and high temperature.](image)

The test solution is introduced into the reactor vessel and closed with the equipment lid, then the safety clamps are located and the clamping screws are tightened. Because the oil well systems have very low or no oxygen concentrations, the N\textsubscript{2} inlet valve is opened to the reactor, the gas passage is maintained for 1 hour to remove the oxygen present in the vessel. After the removal of oxygen, CO\textsubscript{2} injection is performed to the value required by the test, because of this the equipment has an analogy pressure gauge and a pressure sensor. Additional variables such as temperature and flow rate were monitored at the control panel.

At the end of the test, the system is depressurized and the gas is sent out of the laboratory by means of a gas extraction line. The jaws are removed and the lid is removed from the equipment. The electrochemical specimen is disassembled and cleaned with acetone before being labelled and placed in a re-sealable bag with silica gel inside and finally stored in a desiccator for further analysis.

2.1. Electrochemical evaluation
A potentiostat is connected to each of the electrodes to form an electrochemical cell, after 45 minutes of potential stabilization the measurement of resistance to linear polarization and the Tafel polarization curve is performed, then, the Corrosion rate is analysed and determined. Inhibitors usually adsorb on the metal surface, protecting, forming films, reducing corrosive processes by these actions:

- Increasing the anodic or cathodic polarization (Tafel Curves).
- Reducing the movement and diffusion of ions to the metal surface.
- Increasing the electrical resistance of the metal surface [9].

2.2. Efficiency of a corrosion inhibitor
The evaluation of corrosion inhibitors is carried out according to the NACE G 170 standard. The efficiency of a corrosion inhibitor is defined by equation (1) [13]:

\[
\text{Efficiency (\%)} = \frac{V_{\text{corr(blanco)}} - V_{\text{corr(inh)}}}{V_{\text{corr(blanco)}}} \times 100
\]
2.3. Materials and methods
The basic assembly of a test consists of the preparation of the solution, with distilled water and the addition of nitric acid or sodium hydroxide, according to the required value. The experimental units are cylindrical API N80 steel pieces, with an area of 2.2cm².

2.4. Variables chosen and their values to perform the tests
Tests will be carried out to complete the parametric control, taking into account the chosen levels, in a random way by submitting the treatments with each level of variable shown in Table 1.

| Variables | Pressure CO₂ (psi) | Temp. (°C) | pH | Flow rate (m/s) | Dosage (ppm) |
|-----------|------------------|-----------|----|----------------|-------------|
| Levels    | 300              | 40        | 4  | 0              | 20          |
|           | 500              | 80        | 8  | 0.5            | 50          |

2.5. Mathematical model
The regression model is a fractional factorial design, which predicts the effectiveness of the inhibitor for the established ranges. A final number of 32 tests was obtained, however 16 tests were taken; Measuring the effect of each of the variables, using coded data, for high levels it is tabulated as 1 and for low levels as -1.

3. Results and discussion
Thirty-two tests were performed in which the total combinations were completed, and tests were performed without inhibitor or blank solution to determine dosing efficiency. According to Table 2, for the first 8 tests the parameters were fixed (TEMP 40°C, PH 4); For tests 9-6 (TEMP 80, PH 4); 17 to 24 (TEMP 40°C, PH 8) and from test 25 to 32 (TEMP 80, PH 8).

Table 2. Results.
| No. | a    | b    | c    | d    | e    | No. | a    | b    | c    | d    | e    |
|-----|------|------|------|------|------|-----|------|------|------|------|------|
| 1   | 300  | 20   | 0    | 69.83| 70.59| 17  | 300  | 20   | 0    | 56.04| 56.13|
| 2   | 300  | 20   | 0.5  | 69.52| 70.86| 18  | 300  | 20   | 0.5  | 55.93| 56.40|
| 3   | 300  | 50   | 0    | 70.67| 68.95| 19  | 300  | 50   | 0    | 57.64| 57.74|
| 4   | 300  | 50   | 0.5  | 70.11| 69.23| 20  | 300  | 50   | 0.5  | 57.12| 57.02|
| 5   | 500  | 20   | 0    | 65.31| 65.90| 21  | 500  | 20   | 0    | 54.29| 51.44|
| 6   | 500  | 20   | 0.5  | 63.57| 66.17| 22  | 500  | 20   | 0.5  | 52.73| 51.71|
| 7   | 500  | 50   | 0    | 68.5 | 67.67| 23  | 500  | 50   | 0    | 54.42| 55.46|
| 8   | 500  | 50   | 0.5  | 68.16| 67.95| 24  | 500  | 50   | 0.5  | 54.28| 55.74|
| 9   | 300  | 20   | 0.5  | 85.18| 85.11| 25  | 300  | 20   | 0.5  | 61.83| 62.11|
| 10  | 300  | 20   | 0    | 84.78| 82.60| 26  | 300  | 20   | 0    | 60.96| 59.60|
| 11  | 300  | 50   | 0    | 87.02| 83.47| 27  | 300  | 50   | 0    | 62.29| 62.73|
| 12  | 300  | 50   | 0.5  | 85.9 | 80.97| 28  | 300  | 50   | 0.5  | 60.54| 60.22|
| 13  | 500  | 20   | 0    | 79.86| 80.42| 29  | 500  | 20   | 0    | 56.73| 57.42|
| 14  | 500  | 20   | 0.5  | 78.17| 77.91| 30  | 500  | 20   | 0.5  | 56.39| 54.91|
| 15  | 500  | 50   | 0    | 83.25| 82.19| 31  | 500  | 50   | 0    | 58.8 | 61.45|
| 16  | 500  | 50   | 0.5  | 79.58| 79.69| 32  | 500  | 50   | 0.5  | 58.71| 58.94|

a: Pressure CO₂ (psi)
b: Dosage (ppm)
c: Flow rate (m/s)
d: Efficiency obtained experimentally (%)e: Efficiency obtained in the mathematical model (%)
3.1. Characterization of corrosion products
The corrosion products found after each test without inhibitor have an opaque and black-grey colour. Specimens that were tested with inhibitor did not evidence adherence of corrosion products. The final appearance of the specimens is presented in Figure 2.

![Figure 2. Final appearance of the specimen. (a) Test without inhibitor and (b) Test with inhibitor.](image)

The absence of orange or reddish tones indicates that there is no significant formation of oxides, indicating that CO\textsubscript{2} and N\textsubscript{2} injection adequately displaced the oxygen from the test solution.

3.2. X-ray diffraction analysis
X-ray diffraction was applied with flush film technique to obtain information on the chemical composition of the corrosion products. Table 3, presents the products and elements identified.

| Element or Compound  | Chemical formula |
|----------------------|------------------|
| Iron carbonate (Siderite) | FeCO\textsubscript{3} |
| Magnetit             | Fe\textsubscript{3}O\textsubscript{4} |
| Iron                 | Fe               |

The result obtained in the X-ray diffraction was the presence of corresponding peaks with siderite, which is an iron carbonate type (FeCO\textsubscript{3}). The detected iron carbonate is the characteristic product of corrosion in aqueous environments with CO\textsubscript{2} at the pH, temperature and pressure levels used. There is presence of magnetite (Fe\textsubscript{3}O\textsubscript{4}).

3.3. Mathematical model
According to the obtained results, a model is established by means of fractional factorial design, that allows to predict the efficiency of inhibitor N-Phenyl Nitrone, to the conditions evaluated. Each of the variables studied has a direct influence on the protective behaviour of the inhibitor on the metal surface, and the model obtained with each of its coefficients is defined by equation 2.

\[
\% Efficiency = 74.4795 - 0.0348166 \times P_{CO_2} - 0.185835 \times T + 5.76374 \times pH - 0.30025 \times Dosis + 6.105 \times Flow\ rate + 0.0005683 \times P_{CO_2} \times Dosis - 0.053343 \times T \times pH + 0.0018791 \times T \times Dosis - 1.39 \times pH \times flow\ rate
\]  

(2)

3.4. Effect of each variable
Table 4 shows the analysis performed on each of the independent variables, and with each of their combinations that have an effect on the protective behaviour of the inhibitor.

The model allows defining that for this type of inhibitor, the variable that has a significant effect on the inhibitor behaviour is the temperature and the combination between pH and temperature is more influential, for the positive data have a directly proportional effect is shown and in the negative data its effect is inversely proportional to the efficiency.
Table 4. Effect results of the variables. Value of each variable and effect of combinations between variables.

| Effect            | Value | Combination Effect | Value | Combination Effect | Value |
|-------------------|-------|--------------------|-------|--------------------|-------|
| CO₂               | -3.0  | CO₂ - Temperature  | -0.5  | Temperature - Dosage| 0.3   |
| Temperature       | -17.6 | CO₂ - pH           | 0.2   | Temperature - Flow rate| 1.1  |
| pH                | 8.9   | CO₂ - Dosage       | 1.7   | pH – Dosage        | -0.5  |
| Dosage            | 1.2   | CO₂ - Flow rate    | 0.6   | pH – Flow rate     | -1.4  |
| Flow rate         | -1.1  | Temperature – pH   | -4.3  | Dosage – Flow rate | -0.6  |

4. Conclusions

The N-PHENYL-NITRONE molecule has a good protective behaviour in the evaluated conditions, however a reduction of the barrier characteristic is evidenced by the presence of more aggressive conditions.

Iron oxide corrosion products were generated, characteristic of environments rich in CO₂ in the aqueous phase, in basic pH the siderite film is stronger.

The molecule can be applied in high temperature systems. Although it shows a degradation, a protective characteristic is evidenced. Under static conditions the inhibitor tends to behave better, because there is no dynamic agent that can affect adhesion.

The obtained model presents a reliability of 97%, for the ranges studied.

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