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EFFECT OF CONCENTRATION, STIRRING AND TEMPERATURE ON CORROSION BY NAPHTHENIC ACID IN A335-P5 STEELS USING THE ELECTROCHEMICAL NOISE TECHNIQUE

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Abstract. During the oil refining process, the equipment is exposed to the action of compounds such as sulfides, chlorides and carboxylic acids present in the oil. The choice of materials used to perform the design of a refinery or a petrochemical plant considers the different compounds present in petroleum, but the different compositions present in the oils from different parts of the world make this task more complicated, making it even more difficult to choose materials that can withstand all of these process conditions. The control of corrosion by naphthenic acids is one of the great challenges of refineries that process acid oils. This corrosive process, which mainly affects high temperature circuits in oil refineries can lead to rapid mass loss and equipment failure. Many jobs have been developed for information that minimizes corrosion damage. The objective of this work is to analyze the effects of agitation and temperature on the kinetics of corrosion by naphthenic acids, using the technique of Electrochemical Noise in solutions of mineral oil and naphthenic acids in various concentrations. The technique of Electrochemical Noise is based on the non-perturbation of the reaction medium, that is, it does not suffer external interferences. They are spontaneously generated current and potential fluctuations in corrosive reactions. Data acquisitions were performed at temperatures of 100 °C (373.15 K), 150 °C (423.15K) and 175 °C (448.15 K) and at rotational speeds of 0 rpm, 200 rpm and 400 rpm. Three cylindrical and solid electrodes were used for the acquisition of electrochemical noise data, two working electrodes (ASTM A335 P5) and one reference electrode (AISI 316). This study proposes the use of the Electrochemical Noise technique as a tool to evaluate an on-line monitoring methodology, allowing a quantitative evaluation of the corrosion rate.

Keywords: Corrosion, Naphtenic Acid, Electrochemical Noise, Petroleum

1. INTRODUCTION

Naphthenic acids are generated in petroleum by bacterial degradation. These attack the paraffin chain by preferentially forming compounds with shorter chain naphthenic and aromatic rings. The action of biodegradation is cited as responsible for the increase of acidic compounds and compounds containing nitrogen and the reduction in paraffinic compounds (ALMEIDA, 2012).

Naphthenic acids are present in many oils in varying amounts and provide a class of contaminants that induce corrosion. Areas especially noted for the production of crude oils containing high concentrations of naphthenic acid have historically included California, Venezuela, India, China and Russia. More recently, these areas have also included some regions not historically known to have high levels of naphthenic acid, which include the North Sea, West Africa, Mexico and also the offshore area of Brazil. (KANE, 2002).

Naphthenic acids promote a type of corrosion called Naphthenic Corrosion. This is observed in specific regions in equipment such as preheaters, furnaces, feed and reflux sections of distillation columns, atmospheric and vacuum

columns, heat exchangers and condensers. These are places where the process temperatures are very high, thus favoring the process of naphthenic corrosion.

Corrosion control strategies should always be implemented in the industry so that the performance and reliability of the operating units are not reduced. The performance of these operating units and the reliability of the system can also be reduced if control strategies such as preliminary assessment, mitigation and monitoring are not implemented.

The corrosion of naphthenic acid occurs mainly in high-speed areas of distillation units and in the temperature range of 220 °C to 400 °C. Generally no damage due to corrosion is found at temperatures above 400 °C, most likely due to the decomposition of naphthenic acids or protection against the coke formed on the surface of the metal. The corrosion by naphthenic acids can be retarded by sulfur-containing compounds inherently present in crude petroleum fractions in the form of soluble sulfides.

The mechanism of naphthenic corrosion consists, basically 4 main steps (QING, 2010):

- Transfer of the molecules of naphthenic acids to the metal surface.
- Absorption of the molecules on the metal surface.
- Reaction with active centers on the surface.
- Desorption of corrosion products.

The reaction process of naphthenic corrosion is described through reactions 1 to 3: (SLAVCHEVA, 1999).



Considering a free surface of protective films, the above reaction implies that in a direct contact of the ligand, the naphthenate ($\text{R}[\text{CH}_2]_n\text{COO}^-$) reacts with an alloy system as FeCrNiMoMn (AISI 316 and 317 stainless steel) causing corrosion of iron. Iron naphthenate $[\text{Fe}(\text{RCOO})_2]$ is oil soluble and its surface is film free. In the presence of H_2S a sulphide film is formed which may provide some protection depending on the acid concentration.

The liquid reaction processes may also apply to chemical or electrochemical reactions. The distinction with respect to the latter is that there are separate anode and cathodic reaction processes with ion movement through the solutions and electrons of the metal.

2. METHODOLOGY

In this work, a cylindrical closed vessel type reactor was used, which was called an Electrochemical Reactor, machined in a 6351 aluminum alloy. The reactor heating was performed by an electric resistance jacket installed externally to the reactor and the control of temperature was done through a microcontroller coupled to a type "J" thermocouple internally to the reactor. A corrosion probe type was coupled to the central hole of the reactor cover. This probe has in its upper part connections that connect the cables that detect the electrochemical data generated during the experiment. At the bottom of the corrosion probe are connected two working electrodes, made of A335 P5 solid steel, and a reference electrode in AISI 316 stainless steel, also massive. The corrosive process was evaluated in a solution containing mineral oil and three solutions containing mineral oil with a certain concentration of naphthenic acids. The objective was to analyze the concentrations similar to those found in petroleum processed as follows:

- $C_{\text{NAT}} = 0.0$ mg KOH / g, obtained as reference of zero corrosion by naphthenic acids;
- $C_{\text{NAT}} = 2.5$ mg KOH / g, simulating stabilized petroleum;
- $C_{\text{NAT}} = 8.0$ mg KOH / g, simulating petroleum derivatives at the lower outlets of the distillation columns, where there is an increase in the concentration of naphthenic acids;
- $C_{\text{NAT}} = 28.0$ mg KOH / g, simulating condensation regions of vapors rich in naphthenic acids in the interior of distillation towers.

The experiments were performed without stirring at rotational speeds of 200 rpm and 400 rpm and at temperatures of 100 °C (373.15 K), 150 °C (423.15K) and 175 °C (448.15 K). Data collection was acquired at 10-minute intervals.

The electrochemical noise data was recorded through Gamry Instruments ZRA Reference 600 Potentiostat/Galvanostat.

The frequency of operation was 500 Hz and the data acquisition was 10 Hz. The current noise data were treated and evaluated as the reaction charge density (q in C/cm^2) involved in the corrosive process and obtained by relationship:

$$q = \int i \, dt \quad (1)$$

where "i" is the electric current density, in A/cm^2 , and "dt" is the time interval analyzed, in seconds.

3. RESULTS AND DISCUSSIONS

The reaction loads involved in the corrosive processes were calculated from the current noise graphs and Equation 1. After analyzing the results the surface plots shown in Figures 1, 2, 3 and 4 were reached.

It is observed that the reaction load involved in the corrosive process increases in the four cases studied.

This behavior is in agreement with the expected one, since the dissociation of the naphthenic acids in $R-(CH_2)_nCOO^-$ and H^+ is increased with the increase of the temperature, accelerating the reactions of electrochemical corrosion. However, there is still the influence of the agitation of the system, which contributes to the greater contact of the naphthenate ions with Fe^{2+} ions, further increasing the corrosive process.

Figure 1 shows that, even without naphthenic acid addition, an increase in corrosivity was observed when compared with temperature and agitation. This fact is probably due to the influence of parallel reactions due to the degeneration of the mineral oil used. New experiments must be performed to prove this fact.

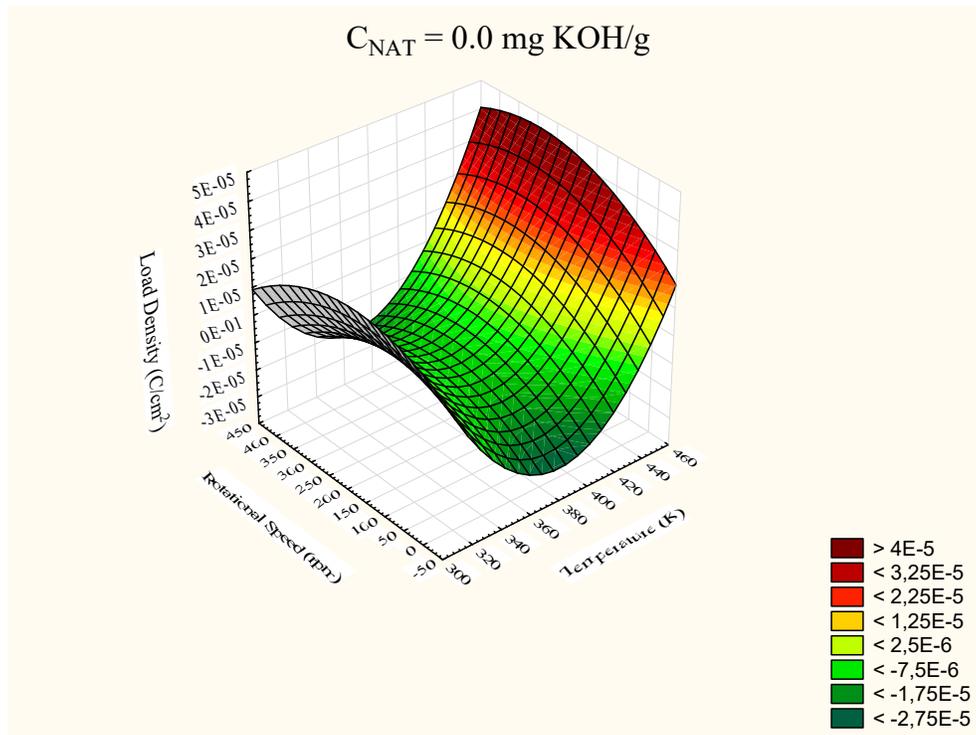


Figure 1: Total Reaction Load (C/cm^2) versus Temperature (K) and Rotational Speed (rpm) for $C_{NAT} = 0,0 \text{ mg KOH/g}$.
Reference: The Author

All the experiments show a small decay of the corrosivity with the increase of temperature at the beginning of the process and that with the increase of the temperature, this returns to increase. This fact is due to the dissolved oxygen present in the solution. When the system temperature is increased, this oxygen is eliminated.

Comparing Figures 2, 3 and 4, when the concentration of naphthenic acids increases, the corrosiveness increases in the ratio of 10 times between the concentration of $C_{NAT} = 2.5$ and $C_{NAT} = 8.0 \text{ mg KOH / g}$ also for the concentrations of $C_{NAT} = 2.5 \text{ mg KOH / g}$ and $C_{NAT} = 28.0 \text{ mg KOH / g}$.

When comparing the temperature with the agitation, this prevails for the increase of the corrosiveness of the system in all the concentrations studied.

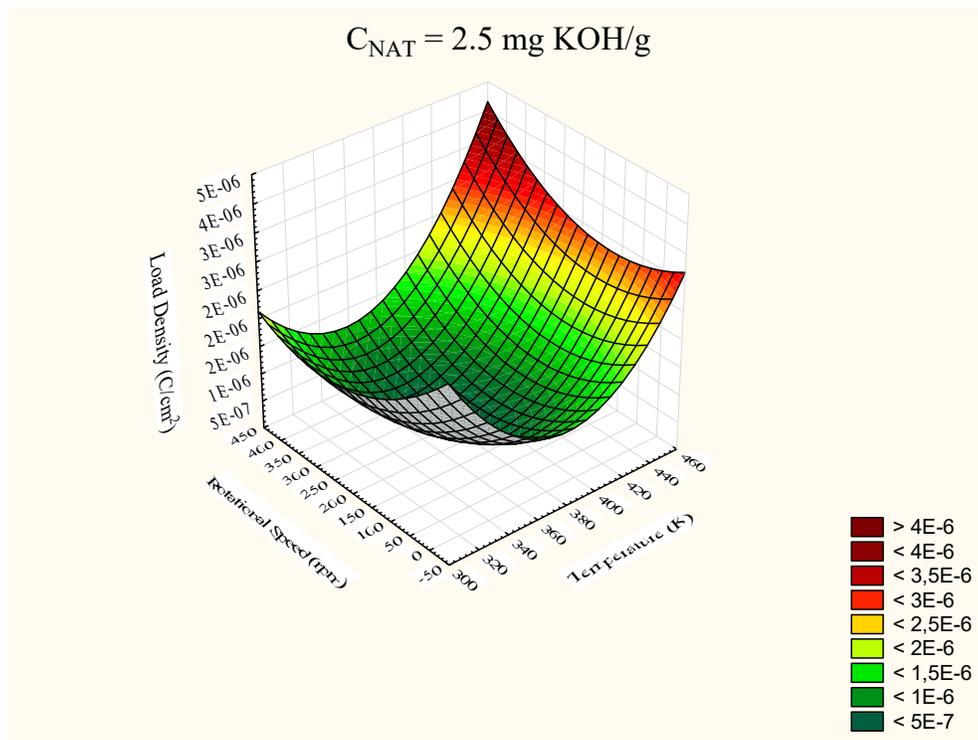


Figure 2: Total Reaction Load (C/cm^2) versus Temperature (K) and Rotational Speed (rpm) for $C_{NAT} = 2,5 \text{ mg KOH/g}$.
Reference: The Author

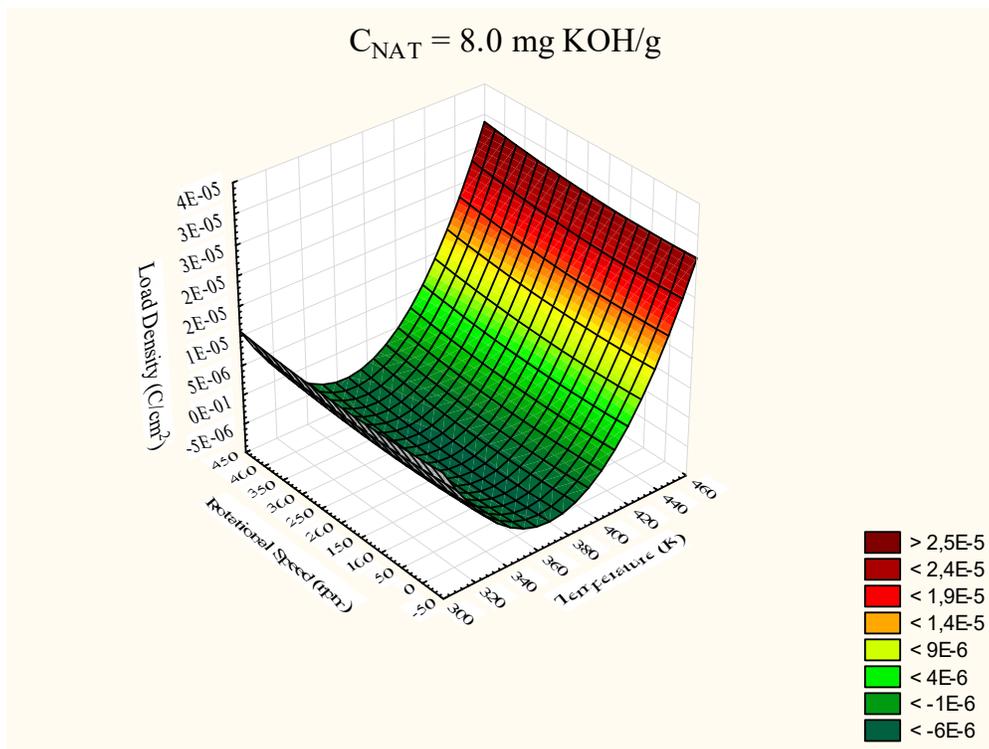


Figure 3: Total Reaction Load (C/cm^2) versus Temperature (K) and Rotational Speed (rpm) for $C_{NAT} = 8,0 \text{ mg KOH/g}$.
Reference: The Author

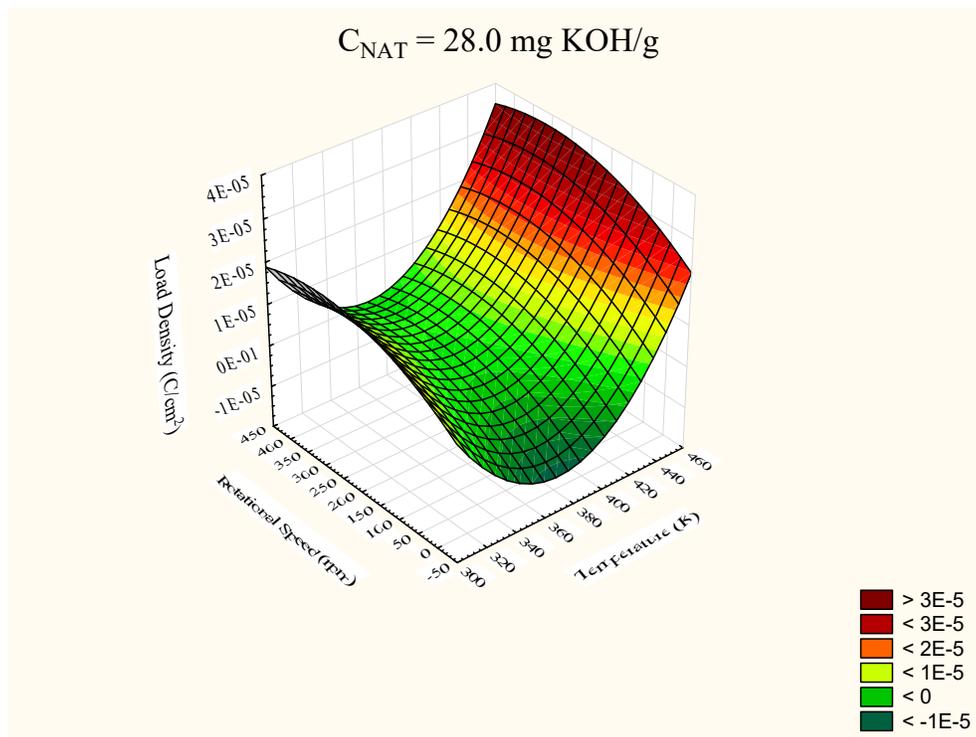


Figure 4: Total Reaction Load (C/cm²) versus Temperature (K) and Rotational Speed (rpm) for $C_{\text{NAT}} = 28,0 \text{ mg KOH/g}$.
Reference: The Author

4. CONCLUSIONS

The Electrochemical Noise technique has been shown to be sensitive to changes in the variables studied in this work. It was possible to verify by the technique of Electrochemical Noise that, by the analysis of the load density, in addition to the influence of the temperature, there is a significant influence in the corrosive process when a stirring is added in the reaction system. In addition, it has been found that increasing the concentration of naphthenic acids also contributes to increased corrosivity.

5. ACKNOWLEDGEMENTS

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