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# Evaluation of naphthenic acidity number and temperature on the corrosion behavior of stainless steels by using Electrochemical Noise technique

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ABSTRACT

The processing of heavy oils in Brazilian refineries has exposed the equipment to more severe corrosive processes, mainly due to the presence of contaminants. The naphthenic acids can be quoted as an example of these contaminants, which are made of organic acids saturated rings and one or more carboxylic groups. Consequently, refiners are adjusting their metallurgy facilities and investing in real time instrumentation for monitoring the corrosion rates, thus enabling the optimization of the consumption of opportunity crude oils and dosing of anti-corrosive products. As an alternative to commonly used techniques for corrosion monitoring, such as weight loss coupons and electrical resistance probes, studies are being conducted to evaluate and validate the use of the Electrochemical Noise technique in oily media. This method has proven to be the most appropriate for high ionic strength solutions, as the case of oil, corrosive and it is proven to be sensitive for corrosion processes caused by naphthenic acids. This study aims to evaluate the influence of temperature – 25 °C, 65 °C and 120 °C – and the total acidity number (TAN) – 0.5, 1.5 and 2.5 mg KOH/g – in the naphthenic acid corrosion in austenitic stainless steel type 316. An electrochemical reactor consisting of three identical electrodes of 316 stainless steels roads, with an area of 8.95 $cm^2$ for each electrode, was used to evaluate the corrosive process, along with electrolytes consisting of pure mineral oil and mineral oil with naphthenic acids. The Electrochemical Noise technique was applied in the first 5 h of contact between the electrodes and the electrolyte, with a frequency of 10 Hz acquisition. As a result, it was observed that when the temperature or the TAN increase, both the susceptibility of the 316 steel to general corrosion and the incidence of localized corrosion also increase. Meanwhile, the temperature effect was more significant in the studied conditions. Besides, the Electrochemical Noise technique demonstrated sensitivity to identify corrosive process variations even in conditions considered to be of very low severity.



## 1. Introduction

The naphthenic corrosion control is one of the biggest challenges of the refineries in Brazil that process heavy oils. Its monitoring aims to evaluate the effectiveness of a corrosion control program and the establishment of operational limits, and to provide alarms for corrosive behavior changes, providing information to adjust the program. Many works have been developed in search of information on critical operating parameters and monitoring methodologies, but few provide an online predictive and proactive control for the corrosive process.

Facing the need to make online control methods more suited to industrial reality, this paper proposes the use of Electrochemical Noise (EN) as an assessment tool of some proposed control parameters and the monitoring of corrosion by naphthenic acids.

Among the many problems with corrosion in oil refineries, the naphthenic corrosion must be addressed. It is caused by the activation of the naphthenic acid at high temperatures during the refining of petroleum [1–3,16].

The naphthenic corrosion is an electrochemical process that occurs in the liquid fractions of the petroleum in the temperature range occurring in the refining units. The corrosion occurs in the anodic areas of the metal with the generation of hydrogen at the cathodic areas [17]. An important aspect that must be considered is that the acid tends to dissociate into R-$(CH_2)_n$-$COO^-$ and $H^+$ even in organic liquid media [3,13,18].

In situ and laboratory observations demonstrate that corrosion by naphthenic acids is influenced by several parameters, such as the

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temperature, speed and physical condition of the fluid, the composition of the oil pressure and building materials. In this paper, it was evaluated the influence of temperature and total acidity number (TAN) of oil [3].

Regarding the influence on the temperature, corrosion by naphthenic acids occurs in carbon steels, low alloy steels, austenitic stainless steel AISI 316 and AISI 410 steels in the temperature range of 200–400 °C [4], the same temperature range for the boiling of the naphthenic acid. The process is most severe at the interface vapor/liquid in regions where condensation occurs on the metal surface at temperatures below the boiling or condensation of acid [3].

Recently some studies have proven the high corrosivity of acidic fractions of kerosene at temperatures below 200 °C. Traditionally, naphthenic acid corrosion is not pronounced in fractions lighter than diesel in atmospheric distillation columns, so these cases are considered as "naphthenic corrosion at low temperatures" [5].

There is another very relevant parameter when dealing with naphthenic corrosion: the total acidity number (TAN). This parameter indicates the number of all kinds of acids present in the sample and may be a naphthenic acid or inorganic acids [6] and is determined by titration with KOH, representing the amount of KOH required, in milligrams, to neutralize the constituent acids present in one gram of sample [13]. The analysis was performed as described by ASTM D974 standard for the colorimetry method, and D664 standard for the potentiometric method [3,13].

The petroleum has been considered acid with a TAN values higher than 0.5 mg KOH/g for the crude. In this range the corrosion by naphthenic acids occurs depending on the operating temperature, resulting from the vaporization of naphthenic acids and subsequent condensation on the equipment surface [7].

Jayaraman affirms that some types of oil have activation of the naphthenic acid in TAN in the range of 0.3 mg KOH/g crude. However, the naphthenic corrosion is more pronounced for TANs above 1.5 mg KOH/g crude. Above 1.5 mg KOH/g crude, the corrosion rate typically varies linearly with the TAN, nevertheless there may be exceptions [1–8].

There are many ways to monitor and reduce the damage caused by naphthenic acids. A technique recently studied in scientific papers, and that may be the solution for the monitoring of corrosive processes in real time, is the Electrochemical Noise technique [1]. Electrochemical Noises are spontaneous fluctuations of current and potential presents in a system due to a corrosive process. These fluctuations, if registered, can be studied and they provide a method to estimate the corrosion rate, as well to evaluate the type of corrosion process that is occurring [9].

Several studies indicate that this technique is able to distinguish from general corrosion to localized corrosion, providing an estimate of the corrosion rate without external perturbation of the corrosion system. Each type of corrosion, it may be generalized or localized, has a characteristic behavior of the signal noise. This characteristic behavior can be used as a tool to predict the type of corrosion process that the metal is suffering [9,10,12,14,15].

The first parameter that can be obtained using data acquired during experiments using the Electrochemical Noise technique is the noise resistance $R_n$ [11]:

$$\frac{\sigma_E}{\sigma_I} = R_n$$

where $\sigma_E$ is the standard deviation of the values of potential and $\sigma_I$ is the standard deviation of the values of current. This parameter, although important, does not provide direct information about the corrosion process that is happening.

To achieve this goal, several parameters are proposed in literatures that supposedly are able to present different behaviors when the process is generalized or localized corrosion. One may quote the coefficient of variation of the current, the index location, the kurtosis, among others [15]. In 2001, Cottis made a profound analysis of these parameters and, in 2004, Al-Mazeedi and Cottis indicated that only two of these actually differ for the two types of corrosion cited: the characteristic charge and frequency of events, previously known as the characteristic frequency $f_n$ [9,12].

It is possible to estimate the $f_n$ from the data of potential noise and current noise obtained by the experiments and the set of equations below [12].

$$I_{corr} = \frac{B\sigma_I}{\sigma_E}$$

$$q = \frac{\sigma_I \sigma_E}{Bb}$$

$$f_n = \frac{I_{corr}}{q} = \frac{B^2 b}{\sigma_E^2}$$

where $I_{corr}$ is the average corrosion current, $q$ is the characteristic charge, $\sigma_E$ is the standard deviation of the potential noise, $b$ is the range of measurement of the experiment, and $B$ is the Stern-Geary coefficient.

In practice, as Sánchez-Amaya explained in 2007, the $q$ is associated with the mass of metal lost in the corrosive events, while $f_n$ informs about the rate at which these events are happening [14].

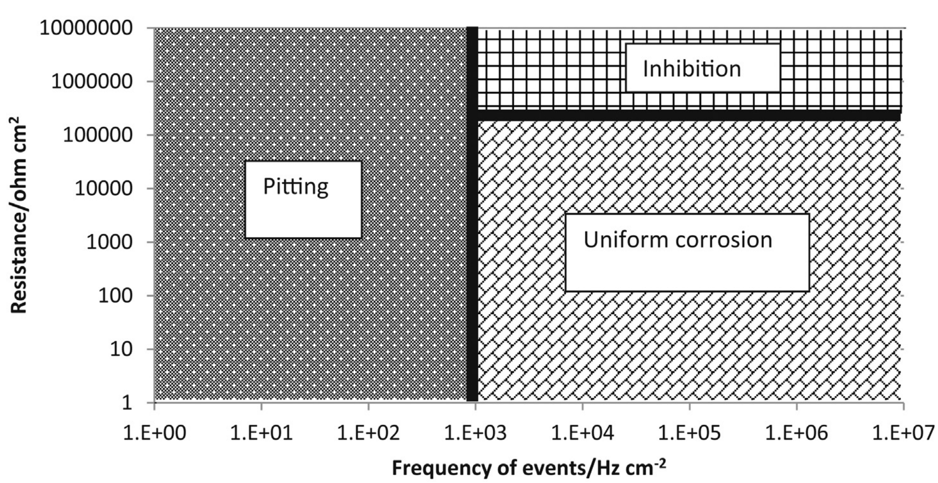


**Fig. 1.** Schematic of $R_n$ vs. $f_n$ showing the classification of types of corrosion.