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(Organizador)

Estudos (Inter) Multidisciplinares nas Engenharias 2

Atena Editora
Ano 2019

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2019

Editora Chefe: Profª Drª Antonella Carvalho de Oliveira
Diagramação: Geraldo Alves
Edição de Arte: Lorena Prestes
Revisão: Os Autores

Dados Internacionais de Catalogação na Publicação (CIP)
(eDOC BRASIL, Belo Horizonte/MG)

E82 Estudos (inter) multidisciplinares nas engenharias 2 [recurso eletrônico] / Organizador Helenton Carlos da Silva. – Ponta Grossa, PR: Atena Editora, 2019.

Formato: PDF
Requisitos de sistema: Adobe Acrobat Reader
Modo de acesso: World Wide Web
Inclui bibliografia
ISBN 978-85-7247-701-7
DOI 10.22533/at.ed.017190910

1. Engenharia – Pesquisa – Brasil. I. Silva, Helenton Carlos da.

CDD 658.5

Elaborado por Maurício Amormino Júnior – CRB6/2422

Atena Editora
Ponta Grossa – Paraná - Brasil
www.atenaeditora.com.br
contato@atenaeditora.com.br

Ano 2019

APRESENTAÇÃO

A obra “*Estudos (Inter) Multidisciplinares nas Engenharias”* aborda uma série de livros de publicação da Atena Editora, em seu I volume, apresenta, em seus 21 capítulos, discussões de diversas abordagens acerca da importância da (inter) multidisciplinaridade nas engenharias.

O processo de aprendizagem, hoje em dia, é baseado em um dinamismo de ações condizentes com a dinâmica do mundo em que vivemos, pois a rapidez com que o mundo vem evoluindo tem como chave mestra a velocidade de transmissão das informações.

A engenharia praticada nos dias de hoje é formada por conceitos amplos e as situações a que os profissionais são submetidos mostram que esta onda crescente de tecnologia não denota a necessidade apenas dos conceitos técnicos aprendidos nas escolas.

Desta forma, os engenheiros devem, além de possuir um bom domínio técnico da sua área de formação, possuir domínio também dos conhecimentos multidisciplinares, além de serem portadores de uma visão globalizada.

Este perfil é essencial para o engenheiro atual, e deve ser construído na etapa de sua formação com o desafio de melhorar tais características.

Dentro deste contexto podemos destacar que uma equipe multidisciplinar pode ser definida como um conjunto de profissionais de diferentes disciplinas que trabalham para um objetivo comum.

Neste sentido, este livro é dedicado aos trabalhos relacionados aos estudos da (inter) multidisciplinaridade nas engenharias, com destaque mais diversas engenharias e seus temas de estudos.

Os organizadores da Atena Editora agradecem especialmente os autores dos diversos capítulos apresentados, parabenizam a dedicação e esforço de cada um, os quais viabilizaram a construção dessa obra no viés da temática apresentada.

Por fim, desejamos que esta obra, fruto do esforço de muitos, seja seminal para todos que vierem a utilizá-la.

Helenton Carlos da Silva

SUMÁRIO

CAPÍTULO 16

RE-EVALUATION OF THE INFLUENCE OF TEMPERATURE AND TOTAL ACID NUMBER ON NAPHTHENIC CORROSION BY ELECTROCHEMICAL NOISE TECHNIQUE

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ABSTRACT: The control of corrosion by naphthenic acids is one of the biggest challenges of the refineries that process viscous oil. This corrosion process, which mainly affects the circuits of elevated temperatures, can cause rapid mass loss and hardware failures. Its monitoring enables the evaluation of the effectiveness of a corrosion control program and the establishment of operational limits. Among the used techniques, there is the monitoring of the composition of the streams of crude oil and the measurement of corrosion rate (mass loss coupons, electrical resistance, ultrasound, etc.). Many researches have been developed aiming both information on critical operating parameters and new methods of monitoring, but there are few options that provide online predictive and proactive control of the corrosive process. This research proposes the use of the use of Electrochemical Noise technique as an evaluation tool control parameters and monitoring corrosion by naphthenic acids in critical process conditions. ASTM A335 P5 material was evaluated in oily media with total acid numbers (NAT) of 2.5, 8.0 and 28.0 mgKOH/g at temperatures between 100 °C to 250 °C. It was observed that, under the studied conditions, the temperature is the predominant variable, inducing increased Reaction Charge with its increase. Moreover, the evaluation of Noise Resistance and Frequency of Events demonstrated that there is a predominance of general corrosion in milder temperatures, with an incidence of localized corrosion above 200 °C.

KEYWORDS: electrochemical noise, corrosion, naphthenic acids, petroleum refining.

1 I INTRODUCTION

A significant amount of heavy oil of low °API, 10-26 °API, (QING, 2010) has been processed in Brazilian refineries due to the existing reserves of this type of oil in our territory and in other regions of the world. Theproportion of world production of this type of oil in relation to the total increased from 11% in 1995 to 14% in 2005 and has grown rapidly in recent years.

This oil is known as opportune due to its low market value, which is around 80% of the value of conventional oil (QING, 2010), with discounts of more than U$ 10/bbl (LU, 2012; GRUBER *et al*, 2012). This devaluation is due to its high viscosity and high density, usually > 930 kg/m^3 (GRUBER *et al*, 2012), in addition to the presence of contaminants such as metals, sulfur and naphthenic acids.

It is known that the sources of crude oil in South America, including Brazil, are among the most acidic crude oils in the world (GRUBER *et al*, 2012) and that its refining has caused severe damage to the equipment. This is mainly because most of the refineries are designed and built for the processing of oils with low levels of naphthenic acids and that currently process the oil due to its economic viability.

The control of corrosion by naphthenic acids is one of the major challenges of refineries processing opportune oils. This corrosive process, which mainly affects high temperature circuits in oil refineries (SLAVCHEVA *et al*, 1999), can lead to rapid mass loss and equipment failure (RECHTIEN, 2006). The most vulnerable unit to naphthenic corrosion is vacuum distillation, since the vacuum heavy Diesel oil tends to have a higher total acidity number. Other critical points are furnace pipes, curves, transfer lines, hulls and plates of the atmospheric distillation column (ALVISI and LINS, 2011; MOURA *et al*., 2012). Possible effects are the loss of thickness in plates and downcomers, where vapor condensates with high acid concentrations, and on the walls of the columns where the condensate flows. Localized attack is also observed, especially in regions where there is poor formation of the iron sulphide film and at high velocity sites, resulting in the process known as corrosion-erosion.

The performance of the operating units and the reliability of the system can also be reduced if appropriate control strategies are not implemented (RECHTIEN, 2006). Thus, evaluation, mitigation and monitoring techniques must be used in order to control the corrosive process caused by naphthenic acids.

Although several works are being developed for a better understanding of the corrosion by naphthenic acids, their nature and the factors that control them have not yet been fully understood. This is due to the complexity and interrelationship of factors that affect corrosion and corrosion-erosion processes, such as total acid number (NAT), naphthenic acid activity, boiling point distribution and decomposition. The process control parameters, such as feed rate and operating temperature, as well as metal susceptibility to corrosion, also make it difficult to clarify how naphthenic corrosion acts for different types of oils (SPEIGHT, 2014).

The evaluation of the corrosive process and its monitoring in high resistivity media, such as desalted petroleum, $10^{13\text{-}16}$ ohm·cm (HASS *et al*, 2013), has been performed through mass loss coupons, solution analysis, galvanic current detection, measurement of electrical resistance and electrochemical measurements (TAN, 2011). In practice, electrochemical corrosion tests on high resistivity media present some challenges. The first one is related to the difficulties with the installation and removal of sensors in areas of difficult access, as well as their configuration and maintenance.

In addition, the auxiliary and reference electrodes maintain a significant potential drop due to the ohmic resistance of the solution and the distribution of non-uniform bias current that may cause uncertainties in the analysis data. The last challenge is related to the limitation of the electrochemical methods to simulate and to measure the localized corrosion, commonly found in high resistivity system.

The corrosion by naphthenic acids occurs predominantly in high oily resistivity oily medium. Regarding the evaluation of this corrosion process, several research methodologies have been presented, mainly based on laboratory tests with autoclaves or loops and on mass loss measurements (HAU *et al*., 2003). This research proposes the application of the Electrochemical Noise (EN) technique for the monitoring of the naphthenic corrosion as an alternative to the evaluation and monitoring processes of the corrosive process in real time. This technique measures the spontaneous fluctuations in current and potential resulting from the charge transfer reactions (TAN, 2011; ABALLE *et al*., 2001; AL-MAZEEDI and COTTIS, 2004; HASS *et al*, 2013).

After the current and potential noise data acquisition, the methods of analysis are divided according to the dependence of the acquisition and recording sequence of the signals. Among the methods that are independent of the reading sequence of the data are the calculations of the statistical moments, such as the mean (first moment), the variance (second central moment) and the standard deviation. The standard deviation is the parameter most commonly used to describe the amplitude of the noise signal (COTTIS, 2001). In this method, it is possible to obtain the Noise Resistance (R_n) from potential and current fluctuations, being defined as the ratio of the standard deviations of potential (σ_E) and current (σ_I) fluctuations.

Al-Mazeedi and Cottis (2004) considered the current to be a series of statistically independent packets of charge, where each packet has a short duration. Under these conditions, three parameters can be obtained: the average corrosion current, I_{corr}; The average charge of each event, q; And the Frequency of Events, f_n. This results in a graph (Figure 1), where: a) high frequency and high resistance indicate generalized corrosion with protective film formation; b) high frequency and low resistance indicate generalized corrosion without protective film formation; c) low frequency indicates localized corrosion.

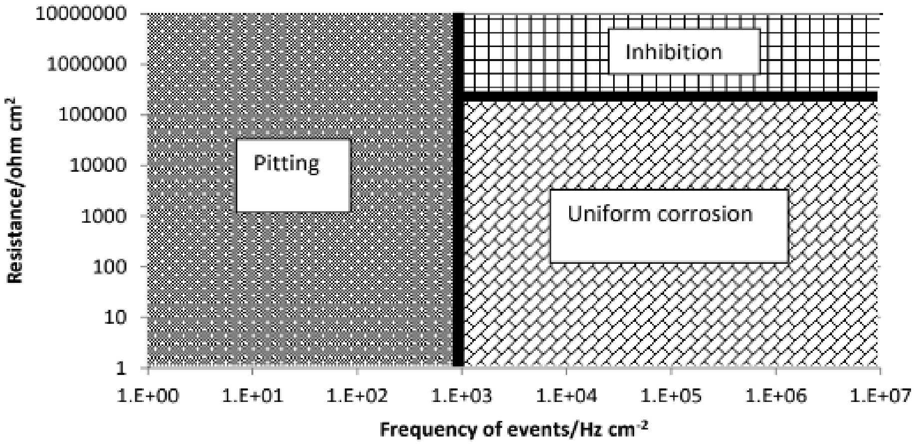

Figure 1 – Graphical representation for the methodology proposed by Al-Mazeedi and Cottis (2004).

Al-Mazeedi and Cottis (2004) methodology lack of an objective analysis, since the results are graphical do not affirm a threshold that can be used as a corrosion type classification. Therefore, aiming for a threshold result, in parallel, current noise was also analyzed through the Noise Reaction Charge (Q in C) involved in the corrosive process. The Noise Reaction Charge was obtained by integrating the curve of the current noise module (I) by time (t), representing the Noise Reaction Charge referring to the current fluctuation between the two working electrodes. Likewise, Corrosion rates were calculated using Faraday's Law.

2 I MATERIALS AND METHODS

For the development of this research, three variables (concentration of naphthenic acids, temperature and electrode material) were chosen.

The corrosive process of three mineral oil solutions with naphthenic acids, similar to the processed petroleum and its derivatives with higher corrosive potential, was evaluated: NAT=2.5 mgKOH/g, simulating stabilized petroleum; NAT=8.0 mgKOH/g, simulating naphthenic acid concentration derivatives; NAT=28.0 mgKOH/g, simulating condensation regions in distillation towers. The reaction media were obtained by adding naphthenic acids (commercial mixture of carboxylic acids alkyl-cyclopentanes) to the mineral oil (liquid vaseline), resulting in solutions with the previous quoted NAT for the three mediums. The NAT of the reactional mediums were confirmed using ASTM D974-08 with a variation of less than 0.5 mgKOH/g. The solutions were previously deaerated with nitrogen for 1 hour and heated at a rate of 75 °C/hour in an electrochemical reactor made from aluminum.

Data acquisitions were performed at temperatures of 100 °C, 150 °C, 200 °C and 250 °C, to comprehend the beginning of the critical range for naphthenic corrosion and the operation range of the equipment with naphthenic corrosion (ALVISI and LINS, 2011; GUTZEIT, 2006; BAGDASARIAN *et al.*, 1996). The pure mineral oil was also analyzed in these temperatures in order to obtain the reference of null corrosion by naphthenic acids under the studied conditions.

The main material evaluated as a working electrode was an ASTM A335 P5 low alloy steel, which is present in most refineries, presenting significant naphthenic acid corrosion rates. As reference, AISI 316 was used because it has a higher resistance to naphthenic corrosion.

Three cylindrical and solid electrodes were used for the acquisition of Electrochemical Noise data arranged as two working electrodes (ASTM A335 P5) and one reference electrode (AISI 316). The electrodes were polished with a 600 MESH sandpaper and degreased with alcoholic solution of potassium hydroxide (KOH). After these procedures, the electrodes were washed with distilled water, dried and connected to the corrosion probe.

The recording of electrochemical noise data was performed using a Gamry Instruments ZRA Reference 600 potentiostat/galvanostat. The frequency of operation used was of 500 Hz and the frequency of acquisition of the data was of 10 Hz. The data of current and potential noise were treated according to the methodology proposed by Al-Mazeedi and Cottis (2004), following the calculation of the Noise Reaction Charge.

3 I RESULTS AND DISCUSSION

Initially, the behavior of the ASTM A335 P5 material in pure mineral oil was evaluated in order to obtain a comparison parameter without naphthenic acidity, being called "white" (NAT=0,0 mgKOH/g). After obtaining the current and potential noise values, it was calculated the Noise Resistance and the Frequency of Events, generating the graph of Figure 2.

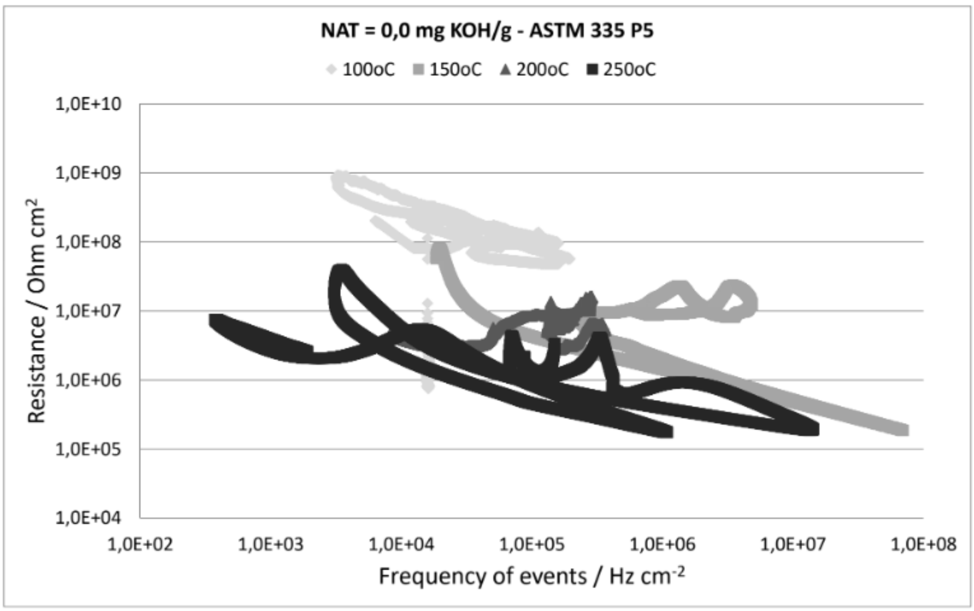

Figure 2 – Noise Resistance vs Frequency of events for ASTM A335 P5 in mineral oil.

According to the interpretation proposed by Al-Mazeedi and Cottis (2004), it is verified that the cluster of points presented a discrete displacement to values of greater Frequency of Events when increasing the temperature of the corrosive medium of 100 °C to 150 °C, indicating a greater tendency to generalized corrosion. For the higher temperatures, the displacement, still discrete, occurred for the region of lower frequency, indicating a greater possibility of occurrence of localized corrosion. However, since there are overlapping point clusters at all temperature conditions in relation to the Frequency of Events, it can be considered that the corrosion is generalized type for all conditions.

When evaluating the Noise Resistance, the experiment indicated reduction of the resistance as the temperature increases, demonstrating the transition from a region of passivation to that of generalized corrosion. During the process of surface treatment of the working electrodes and insertion in the corrosive medium, an oxide layer may have been formed on the surface of the electrodes due to exposure to oxygen from the air. This film was destroyed during the experiment, initiating the process of generalized corrosion without formation of protective film, because it is a medium with low concentration of oxygen.

The Figure 3 exposes the Noise Reaction Charges for ASTM A335 P5 steel in mineral oil. It is possible to observe that there is a gradual increase of the Noise Reaction Charge with as the temperature rises. This behavior was remarkable for the temperature of 250 °C. This indicates a greater intensity in the exchange of electrons between the working electrodes and, therefore, of possible corrosion reactions. This behavior was expected due to the mechanism of peroxidation that the mineral oils undergo when exposed to the heat, forming, among other compounds, acids that collaborate with the corrosive process (OMIDO, 2014).

Regarding the interpretation of the data for the evaluation of ASTM A335 P5 steel in media with NATs 2.5 and 8.0 mgKOH/g, it was observed that the results from the treatment proposed by Al-Mazeedi and Cottis (2004) were similar. The increase in temperature shifted the clusters, in the graph represented in Figure 4 (example), of a region of higher Noise Resistance and lower Event Frequency to another of lower resistance and higher frequency. This behavior demonstrates that at 100 °C temperature, the material still has low corrosive activity on its surface, possibly protected by a protective film of oxide formed during the preparation of the electrode. In addition, naphthenic acids are not as aggressive at this temperature.

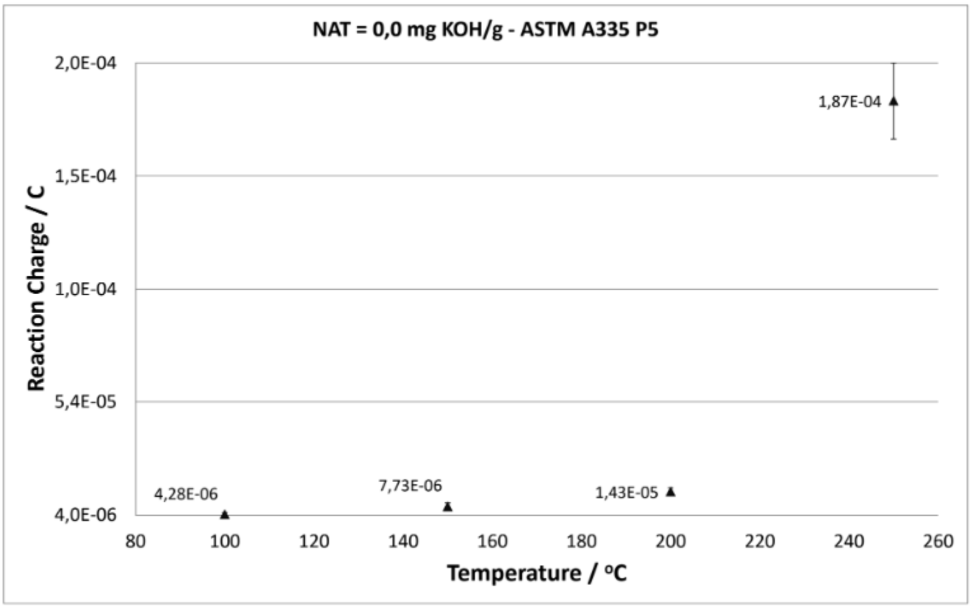

Figure 3 – Noise Reaction Charge for ASTM A335 P5 in mineral oil.

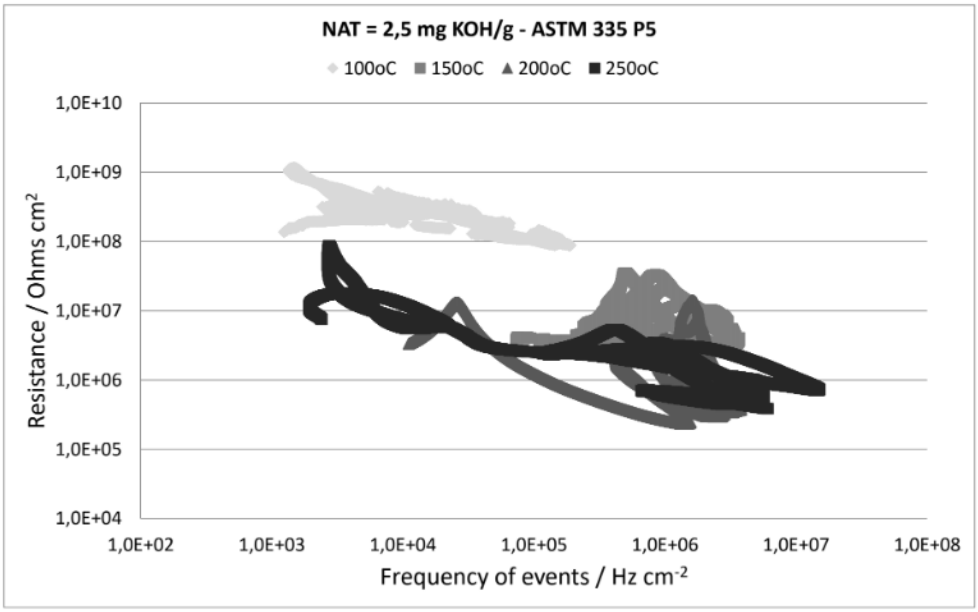

Figure 4 – Noise Resistance vs Frequency of Events for ASTM A335 P5 in solution with NAT 2.5 mgKOH/g.

As the temperature rises to 150 °C, the corrosive process becomes more evident and generalized, characterized by the increase of the Frequency of Events and the reduction of the Noise Resistance. This behavior is in accordance with the literature and with the practical observations for the material studied in non-flow medium, which describe the increase of the corrosion rate with the elevation of temperature and uniform appearance. Between 200 °C and 250 °C, the points shifted to both the region of localized corrosion and localized corrosion, moving to the lower frequency zone. This indicates a possible tendency to pits and alveoli corrosion in this condition, possibly due to the presence of acids.

For the electrolyte with NAT 28.0 mgKOH/g, the calculation of Noise Resistance and Event Frequency (Figure 5) resulted in clusters of points that were exposed for all the analyzed temperatures, demonstrating that the corrosive process is not modified in this situation. Comparing this result with those obtained for less acidic electrolytes, it is observed that the points are located in a region of lower frequency, that is, of localized corrosion.

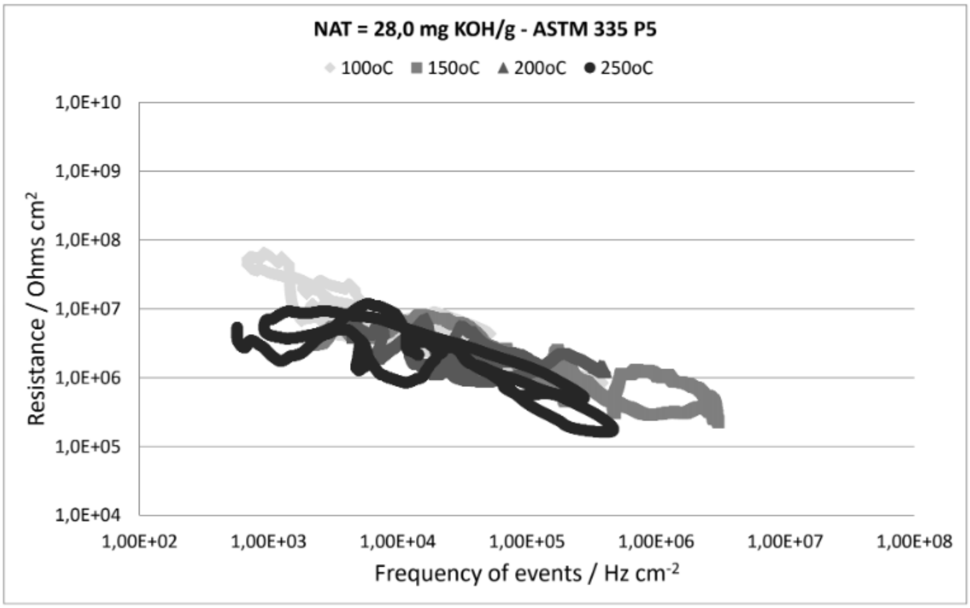

Figure 5 – Noise Resistance vs Frequency of Events for ASTM A335 P5 in solution with NAT 28 mgKOH/g.

For the evaluation of the intensity of the corrosive process, the Noise Reaction Charge involved in each temperature analyzed was calculated from the current noise curves of the experiments described and the values obtained are represented in Figure 6. For the temperatures of 100 °C and 150 °C, the obtained Noise Reaction Charges were in the order of 10^{-5}C, or lower, close to the values obtained for the experiments with pure mineral oil, demonstrating that the corrosive activity due to the presence of naphthenic acids at these temperatures is not significant in these conditions, as expected.

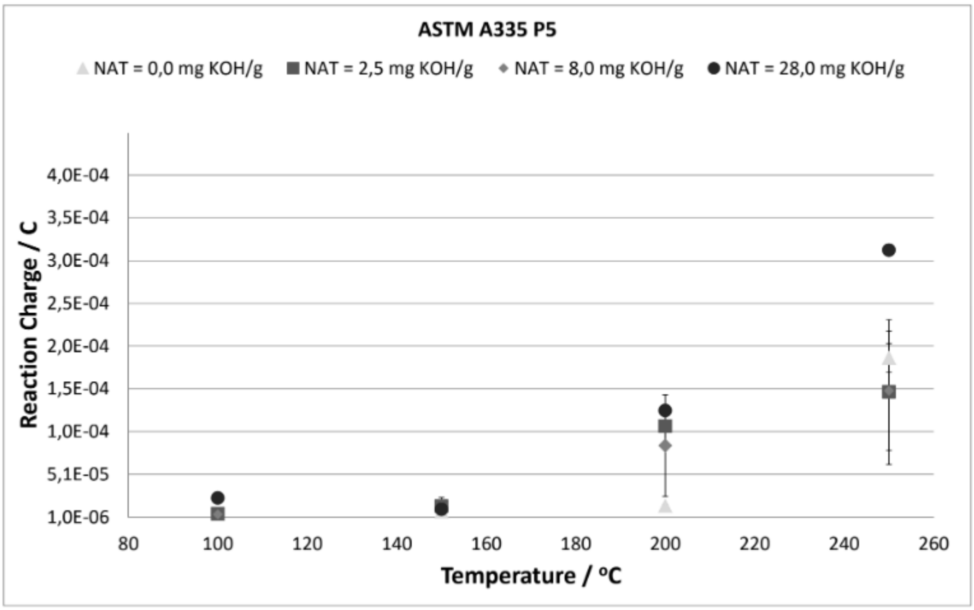

Figure 6 – Noise Reaction Charge for ASTM A335 P5 for the studied Temperatures and NAT.

For the acquisitions carried out at 200 ºC temperature, it is possible to verify that the value of Noise Reaction Charge obtained for the pure mineral is almost two orders of magnitude lower than the charge values for the acid media, which indicates the detection of the corrosive activity of the naphthenic acids. However, it is not possible to differentiate the corrosion intensity between the different acid concentrations due to the standard deviation found between the experiments, especially in the higher temperatures. The same behavior is observed at 250 ºC, where acid electrolytes equal to or less than 8.0 mgKOH/g showed similar Noise Reaction Charges. In these cases, it is understood that the predominant corrosive agents are the possible acidic compounds formed by the thermal degradation of the mineral oil. Only the electrolyte with NAT 28.0 mgKOH/g differs, which presented higher Noise Reaction Charge at this temperature, evidencing the corrosive effect of naphthenic acids.

4 I CONCLUSIONS

The electrochemical noise technique has been shown to be sensitive in the evaluation of the influence of control variables on naphthenic corrosion in oily media, especially temperature, considering the studied conditions.

The methodology proposed by Al-Mazeedi and Cottis (2004) for the analysis of the electrochemical noise data in the system studied provides information on the type of corrosion (localized or generalized), but it is not possible to quantify the aggressiveness of the corrosive process. In almost all the studied conditions, temperatures below 150 ºC induce a generalized corrosion in the working electrodes, whereas above 200 ºC the localized corrosive process already manifests itself in a significant way.

The proposed methodology for calculating the Noise Reaction Charge showed that it is possible to correlate the increase in corrosion intensity, proportional to the corrosion rate, with the temperature. For temperatures below 150 °C there is no significant corrosion in the system studied, but the action of naphthenic acids is identified at temperatures above 200 °C. However, the same interpretation was not obtained when analyzing the influence of the different concentrations of naphthenic acids in the naphthenic corrosion due to the standard deviation obtained in the experiments. Considering the errors, all concentrations can induce the same value of Noise Reaction Charge in the studied conditions, except for the medium with NAT 28.0 mgKOH/g, which presented Noise Reaction Charge above the other conditions at 250 °C.

5 I ACKNOWLEDGEMENT

The authors are grateful to the PRH-24 Human Resources Program and Petrobras for the PhD funding, and to UFPR for the physical space and resources used.

REFERENCES

ABALLE, A.; *et al*. **Measurement of the Noise Resistance for Corrosion Applications.** Corrosion, vol. 57, n. 1, p. 35-42, 2001.

AL-MAZEEDI, H. A. A; COTTIS, R. A. **A practical evaluation of electrochemical noise parameters as indicators of corrosion type.** Electrochimica Acta, n. 49, p. 2787–2793, 2004.

ALVISI, P. P.; LINS, V. F. C. **An overview of naphthenic acid corrosion in a vacuum distillation plant.** Engineering Failure Analysis, n. 18, p. 1403–1406, 2011.

ASTM D974-08: **Standard Test Method for Acid and Base Number by Color-Indicator Titration.**

BAGDASARIAN, A; *et al*. **Crude unit corrosion and corrosion control.** National Association of Corrosion Engineers (NACE) annual corrosion conference and exposition: water and waste water industries, Denver, CO (United States), 24-29 Mar 1996.

COTTIS, R. A. **Interpretation of Electrochemical Noise Data.** Corrosion, v. 57, n. 3, p. 265-285, 2001.

DETTMAN, H. D.; *et al*. **The influence of naphthenic acid and sulphur compound structure on global crude corrosivity under vacuum distillation conditions.** NACE: Northern Area Western Conference, Calgary-Alberta, 2010.

GUTZEIT, J. **Crude Unit Corrosion Guide: A Complete How-To Manual.** 2nd edition, Process Corrosion Consultants, 2006, USA.

GRUBER, L. D. A.; *et al*. Ácidos naftênicos no petróleo. Química Nova, Vol. 35, No. 7, 1423-1433, 2012.

HASS, F.; *et al*. **Evaluation of Naphthenic Acidity Number and temperature on the corrosion behavior of stainless steels by using electrochemical noise technique.** Electrochimica Acta, v. 124, p. 206-210, 2013.

HAU, J. L.; *et al*. **Measuring naphthenic acid corrosion potential with the Fe powder test.** Revista de Metalurgia, Madrid, v. extra, p. 116-123, 2003.

LU, T. **Challenges in Opportunity Crude Processing.** Nalco. International Conference on "Refining Challenges & Way Forward", April 16-17, 2012, New Delhi.

MOURA, L. B.; *et al*. **Naphthenic Corrosion Resistance, Mechanical Properties and Microstructure Evolution of Experimental Cr-Mo Steels with High Mo Content.** Materials Research, n. 15, v. 2, p. 277-284, 2012.

OMIDO, A. R. **Monitoramento da degradação térmica de óleo mineral isolante de transformador utilizando espectroscopia de absorção e fluorescência UV-VIS.** Doctoral Thesis, Universidade Estadual Paulista, Faculdade de Engenharia de Ilha Solteira, 2014.

QING, W. **Processing high TAN crude: part I.** Petroleum Technology Quarterly, Q4, p. 35-43, 2010.

RECHTIEN, R. **Naphthenic acid corrosion control strategies.** In: AIChE – Chicago Symposium, 2006, Chicago. http://www.aiche-chicago.org/symposium06/abstract.htm, 23/01/2011.

SLAVCHEVA, E.; *et al.* **Review of naphthenic acid corrosion in oil refining.** British Corrosion Journal, v. 34, n. 2, p. 125-131, 1999.

SPEIGHT, J G. **High Acid Crudes.** 1st edition, GPP, Elsevier, 2014, USA.

TAN, Y. **Experimental methods designed for measuring corrosion in highly resistive and inhomogeneous media.** Corrosion Science, n. 53, p. 1145-1155, 2011.

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Agência Brasileira do ISBN
ISBN 978-85-7247-701-7
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