



Full Length Article

In situ characterization of naphthenic corrosion of API 5L X70 steel at room temperature



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HIGHLIGHTS

- The naphthenic corrosion occurred at room temperature.
- Insoluble iron naphthenate in mineral oil was formed on the steel surface.
- The use of *in situ* optical micrographs during the electrochemical experiments.
- The use of *in situ* FTIR to characterize corrosion product.
- The use of *in situ* AFM to study corrosion.

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ABSTRACT

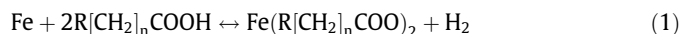
Different *in situ* coupled techniques were used to characterize the naphthenic corrosion of API 5L X70 steel at room temperature. *In situ* optical microscopy coupled with an electrochemical noise technique indicated a general corrosion process. *In situ* AFM images showed the early formation of the corrosion product with a thickness of 600 nm after 90 min of immersion. The main regions observed in the temporal evolution of FTIR spectra are evidence of the formation of an iron naphthenate film even at room temperature.

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1. Introduction

Crude oil containing high concentration of organic acids, such as naphthenic acid, HNap, is produced in different regions of the world. It has been described [1] that, under temperatures higher than 200 °C, the presence of HNap considerably increases the corrosion of steel parts in industrial production units. Therefore, equipment failure has become a critical safety and reliability issue [1–3]. HNap are generally defined as carboxylic acids with one or more saturated ring structures and long chains. Nowadays, linear carboxylic acids also found in oilfields [4,5], such as acetic acid, formic acid and propionic acid, are included in this category [6,7].

Naphthenic corrosion is commonly represented by the following reaction:



where R denotes a hydrocarbon chain. Generally, the corrosion products are soluble in the oil [1,8].

In laboratories, many studies have been performed to mimic the environmental conditions that are observed during metal corrosion caused by petroleum acids in the production units [9–14], including naphthenic corrosion at high temperature [10–14]. However, a small number of papers [15,16] report this type of corrosion at room temperature which is an important issue since these are the environmental conditions where pipelines are installed.

Different methods have been used to study HNap corrosion in oil [1,9]: mass loss, galvanic current detection, electrical resistance, and electrochemical measurements [17]. On the other hand, there

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are few studies which have been done concerning the coupling of electrochemical and other techniques such as optical microscopy, AFM or FTIR. The great advantage of coupled techniques is to follow the metallic corrosion *in situ* together with a second source of information for specific points on the surface [18–20].

Electrochemical noise current and potential fluctuations around the steady state [21] were used to investigate the corrosion under open circuit conditions. The electrochemical noise signal profile (amplitude fluctuations and shape of the transients) is related to the mechanism involved in the corrosion. Hass et al. [15] have recently studied the influence of the temperature and of the total acid number in the naphthenic acid corrosion of austenitic 316 stainless steel using a mixture of mineral oil and naphthenic acids. The electrochemical noise, ECN, was measured during 5 h. It was observed that, as the temperature or the total acid number increased, both the susceptibility of the steel to general corrosion and the incidence of localized corrosion increased, demonstrating that ECN is sensitive enough to identify corrosive changes.

Dias et al. [7] used AFM topography images to study AISI 1020 steel. The authors showed that the naphthenic corrosion in crude oil, with total acid number (TAN) of 0.44 and 4.73 mg KOH g⁻¹, changed after 15 days of exposition. For the steel samples exposed to oil with high total acid number, the appearance of an eroded area on the surface was observed; this eroded area indicates alveolar corrosion which leads to generalized corrosion.

From an experimental point of view, coupling *in situ* optical microscopy with the investigation of the corrosion in crude oil is impossible because the medium is black. However, it is possible to simulate the composition of a crude oil's hydrocarbons using mineral oil, which is transparent, enabling the application of these coupled techniques to such task. To guarantee the experimental condition found in the production units, corrosive agents are also added to the mineral oil. Besides, there is little understanding of the nature of the films that form on steel surfaces during the naphthenic corrosion. The operative corrosion mechanism does not appear to be conclusively identified yet, although some researchers suggest a chemical process. In this sense, Slavcheva et al. [1]

proposed that many of the observations about corrosion by different research groups appear to conflict with each other, and that there is a need for more work to clarify the situation.

Considering the facts exposed above, this study aims to contribute to the characterization of the corrosion product formed on the API 5L X70 steel surface in the presence of organic acids (naphthenic acids, HNap, and acetic acid, HAc) diluted in mineral oil at room temperature. For this purpose we have used temporal series of *in situ* optical micrographs during the electrochemical experiments to obtain information about the development of corrosion, the predominant type of corrosion as well as its intensity. For information about the surface roughness and topography of the film as a function of time, *in situ* atomic force microscopy was also used. Finally, to investigate the chemical composition of the film formed, *in situ* Fourier transform infrared spectroscopy measurements as a function of time were performed. With the combined use of these techniques we were able to obtain important information using a different approach than those described in the literature [15,16] about naphthenic corrosion at room temperature.

2. Experimental

2.1. Materials and electrochemical measurements

The working electrodes were obtained from a pipeline API 5L X70 steel (0.048% Al, 0.14% C, 0.010% Cr, 0.010% Cu, 1.66% Mn, 0.002% Mo, 0.017% Ni, 0.007% P, 0.001% S, 0.16% Si, 0.013% Ti, 0.036% V, balance Fe in wt.%). The microstructure was analyzed using optical microscopy (OM). The metallographic sample preparation for OM observations consisted of grinding using up to 1200-grit paper, followed by polishing with a 0.3 μm aluminum oxide suspension. After polishing, the samples were cleaned with acetone and pure water and then etched. The specimens for general microscopic examinations were etched for 10 s in Nital 2.0%. The micrograph of the API 5L X70 steel metallographic sample, Fig. 1, showed approximately 75% of the ferrite phase with average

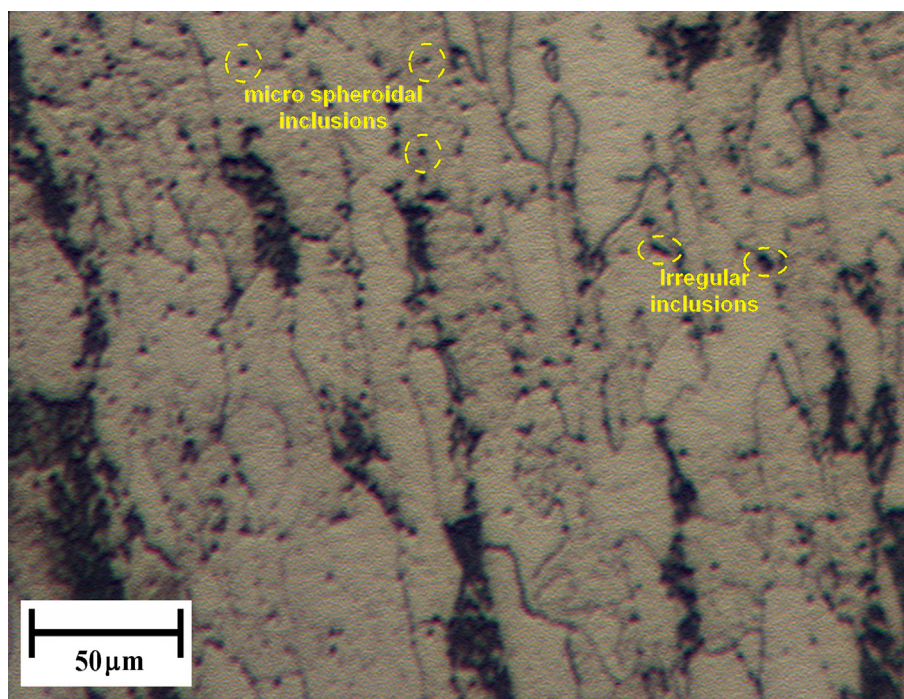


Fig. 1. Metallographic sample of API 5L X70 steel after etching with 2% Nital for 10 s.

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