Optical microscopy coupled to electrochemical techniques to investigate pitting corrosion

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Recently, our group are investigating different aspects of corrosion using optical microscopy coupled to electrochemical techniques. These techniques are used to study aqueous solution with aggressive species such as (Cl^-, H_2S, HS^-, CO_2, Naphtenic acids) which are commonly found in oil industry. Besides, we research also the corrosion in crude oil. In this last case, we use impedance spectroscopy and electrochemical noise. To analyze electrochemical noise results we have used wavelets. It is important also to stress that we use extensively in our research a chemometric approach to perform and interpret the data[1].

Usually, pitting corrosion is investigated using only electrochemical techniques following both, potential and/or faradaic current. The disadvantage of this approach is the lack of information that preserves the spatial coordinates, i.e., that allows to analyze in which point of the surface pit start to grow, once it is well established that current and potential are associated with the sum of all events occurring on the surface at a given period of time. In the literature, *ex situ* images SEM have been used to check the existence of pit corrosion after an electrochemical experiments, as those proposed by Amin *et al.*[2]. Then, we have decided to used both, electrochemical coupled to image acquisition simultaneously in order to preserve both kind of information. To use the images of the corroded surface, at first they have be converted in a appropriated coordinate color systems to perform the corrosion analysis. For example, to study the color texture and shape of a corrosive surface, the images are characterized as color (32 bits)[3,4], or gray scale (8 bits), as in the work of Kapsalas et al [5]. In the case of pit corrosion, the binarized (1 bit) images can be used to separate the background from the object (the pit themselves, in this case)[6]. Of course, the amount of information to be manipulated and, as consequence the computational effort decreases considerably for binarized images. The results allow us to propose model for the kinetic of the pit growth as well as to estimate the pits depth change during the experiments under polarization.

A second technique we have used is the electrochemical noise, EN, technique to study corrosion systems in high resistivity media, such as crude oil. One important difficulty to use conventional electrochemical techniques to investigate this process is the oil itself due its low ionic conductivity which forbids good performing continuous current experiments[7]. To overcome this problem, electrochemical impedance and EN[8], have been proposed as a viable methods. In this last technique the experiments are performed under open circuit conditions, E_{oc}, using two symmetric working electrodes, WE_1 and WE_2, between which the current noise signal, I_n, and the potential noise V_n (against a Pt pseudo-reference electrode, RE) is monitored. To analyze the noise signals we use a mathematical technique still not widely used in this field, the Wavelet Transform[9], with which we can detect, classify and discriminate transient signals even in the case with the superposition of various physical events which occurs with different time constants. The interpretation is generally done using energy distribution plot, EDP, in which it can differentiate the corrosion process. In our studies considering corrosion in crude oil, we take into account the presence of some corrosive species commonly found in this environment such as seawater, naphthenic acid and H_2S. Using a 2^3 factorial design, involving these three species and two values of concentration it was possible to make a correlation between the effect of the three corrosive species and types of corrosion during the experiments. This approach provide the information about the different types of corrosion and which the predominant aggressive chemical specie(s) responsible for this process. This set of electrochemical techniques, mathematical and statistical enabled us to determine the relative weight of the different corrosion processes occurring at the same time which are encoded in a complex signal.

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