Application of the Electrochemical Impedance Technique for the Study and Evaluation of Corrosion in HSLA X65 Steels in a Simulated Environment of Sour Gas H_2S

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Abstract: The main sources for primary energy generation are oil and natural gas, high demand requires the use of pipelines that guarantee transportation in large quantities. Increased use of pipelines, for which it was necessary to develop high-strength steel tubes for long-distance transportation. High-strength, low-alloy steels (HSLA) are a great alternative for transportation, they mechanically resist high pressures and the reduction in manufacturing and maintenance costs is important for large industries. However, in sour gas (H2S) media it may be susceptible to corrosion, therefore studies to assess corrosion resistance are important. The present investigation evaluated the HSLA X65 steel in sour gas media through electrochemical and microstructural characterization techniques, showing its resistance to corrosion in aggressive media and showing that it can be used reliably for the transportation of oil and natural gas.

Keywords: HSLA steels, EIS, oil, H_2S

1. INTRODUCTION

Oil and natural gas are the largest source for the generation of electrical energy consumed in the world today. (1-2) Therefore, there is a high demand to develop -technologies for efficient oil exploration and transportation. Reason for which there is an increase in the manufacture of carbon steel pipes with high mechanical resistance to withstand the operating pressures and environments of oil refineries. (2-4) For the transportation stage, carbon steels are used because they are a structural material with great mechanical properties and low cost, a steel with wide expectations are high-strength, low-alloy carbon steels -HSLA are used for manufacturing. of pipeline manage to resist high pressures, high mechanical and tensile strength, low manufacturing-maintenance costs and excellent weldability. (4-6) The improvement in its properties is mainly due to the addition of microalloying elements Ti, V and mainly Nb. For this reason, HSLA steels are used for the manufacture of bridges, ships, auto parts for vehicles, oil pipelines, whose versatility and the fact that they do not require heat treatment allow great versatility in structural engineering applications. (4-6) Environments of the oil and gas industry, unlike other types of industries, have high concentrations of H_2S (hydrogen sulfide) and CO_2 (carbon dioxide), which reduce the pH of the medium, making it acid, which is why it is called sour gas, these media are considered corrosive and in the wet phase (free water) it facilitates the corrosion and degradation of metallic structures. Whose corrosion damages represent a high budget for maintenance, repair and replacement of material, the most cited damages in the oil industry are hydrogen damages. (6-8) The objective of this research is to determine the behavior and susceptibility to corrosion in the presence of H_2S of HSLA-API 5L X65 pipes, using electrochemical impedance techniques (EIS) as a method or technique. Electrochemical tests (open circuit potential monitoring, electrochemical impedance spectroscopy, and anodic polarization curves) were performed. The electrolyte used is a solution A, following the recommendations of NACE TM0284-16(9), which consists of a solution containing 5% NaCl of acetic acid and 5% NaCl sodium chloride, being studied in three media: in aerated state, washing and saturation H_2S without saturation. Microstructural analysis by optical microscopy (OM) and scanning electron microscopy (SEM) together with X-ray spectroscopy (EDS) energy dispersive analysis.

2. METHODS

For this investigation, a commercial high-strength low-alloy steel HSLA X65 alloy (C: 0.038%, Mn: 0.39%, Nb: 0.085%) was used.

1. **Microstructure analysis:** The microstructure analysis will allow us to know the phases present in our steel, the samples were cut perpendicular to the rolling direction. According to the recommendations of the ASTM E112-2021 standard. (10) To calculate the grain size, they were made with the help of the JPG image program. In order to characterize the microstructure of the samples, they were etched with metallographic reagent-NITAL 2% (2% nitric acid in ethyl alcohol), and again they will be examined by MO and SEM.

2. **Analysis of inclusions:** The analysis of inclusions will allow classifying the inclusions of the study sample, for this the samples were cut parallel to the lamination direction. Following the recommendations of standard E45(2017). (11) The samples of HSLA, steel already cut, were sanded with #100, #320, #600 and #1200 water sandpaper, later they were polished with a suspension of 6µm, 3µm and 1µm diamond paste with an approximate time of 1 minute per cloth. polishing in order to avoid damaging the material. They were then examined by light microscope (OM) and scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) analyzes will also be performed to determine the composition of the inclusions.

3. **Electrochemical tests:** Electrochemical techniques such as open circuit potential-OCP (1500s) and EIS Electrochemical Impedance Spectroscopy (45 min) were used, study of electrochemical behavior under sour gas medium conditions, samples were cut perpendicular to the lamination direction. The electrochemical tests will be carried out in a µautolab type II potentiostat with a frequency analyzer and with the NOVA 1.11 program it will allow the acquisition of the necessary information for the EIS, OCP tests. Tests carried out in deaerated solution A of NACE TM0284 standard. (5% NaCl + 0,5% CH_3COOH), system of three simple electrodes WE: HSLA X65 steel, CE: ECS and CE: Platinum wire. The test parameters were as follows: the electrochemical tests were recorded on a potentiostat (µAUTOLAB type II) coupled to a frequency response analyzer (FRA2). At a frequency scale between 10^{-2} Hz to 10^{5} Hz with an acquisition of 10 points per logarithmic decade and a perturbation amplitude of 10 mV. Data analyzed by Nova 1.1 for data logging and Zview. ASTM G106-89(2015) – Standard. (12)

3. RESULTS

1. Analysis of inclusions and Microstructure analysis

Figure 1 (a-b) shows the results obtained with the examinations by Optical Microscopy-MO and Scanning Electron Microscopy -SEM of the inclusions found in the HSLA X65 tube. The inclusions were examined according to the recommendations of the ASTM E45 (2015) standard. which indicates that they should be examined in the rolling direction. As an image presented by MO, without attack, of the polished surface of the HSLA X65 tube, the inclusions are randomly distributed in the matrix, they present a circular format, chemical analysis complemented for these studies showed that they are rich in Al, Ca and Ti as well as S and Mn. Inclusion size between 2.8 and 9.2 µm. In Figure 4.4 (c) shows results of microstructural analyzes on samples or test bodies cut from the region perpendicular to the rolling direction (ASTM E45). Sanded surfaces up to #1200 and polished up to 1µm, later attacked with metallographic reagent NITAL 2% (2% nitric acid in ethyl alcohol). The presented results of the surface of the HSLA X65 steel indicated a ferrite matrix with and pearlite islands. The Average grain size: 6.5 ± 0.4 µm according ASTM INTERNATIONAL E112−13, 2014.

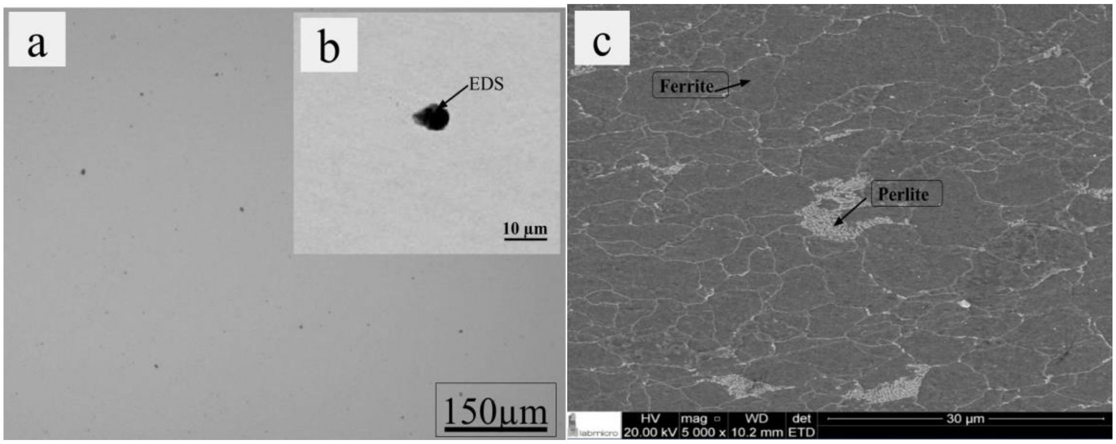

Figure 1. (a-b) Distribution of the inclusions of the HSLA API 5L X65 tube. Polyment 1μm sim attack, 100X MO magnification. (c) SEM microstructural analysis- Nital 2%.

2. Electrochemical tests:

In order to study the effect of H_2S on the electrochemical behavior of HSLA X65 steel, tests were carried out using electrochemical impedance techniques in solution A of the NACE TM 0284-2026 standard, in the presence and absence of H_2S. Figure 2(a) shows the results of the open circuit potential tests (Open Circuit Potential – OCP) as a function of the inversion time. It can be seen that in the presence of H_2S the OCP Potential decreases, becoming more negative (greater activity), results of the electrochemical impedance tests show deformed Nyquist diagrams (Figure 2(b))), whose impedance values decrease in the presence of H_2S, confirming greater susceptibility to corrosion, that is, greater reaction kinetics.

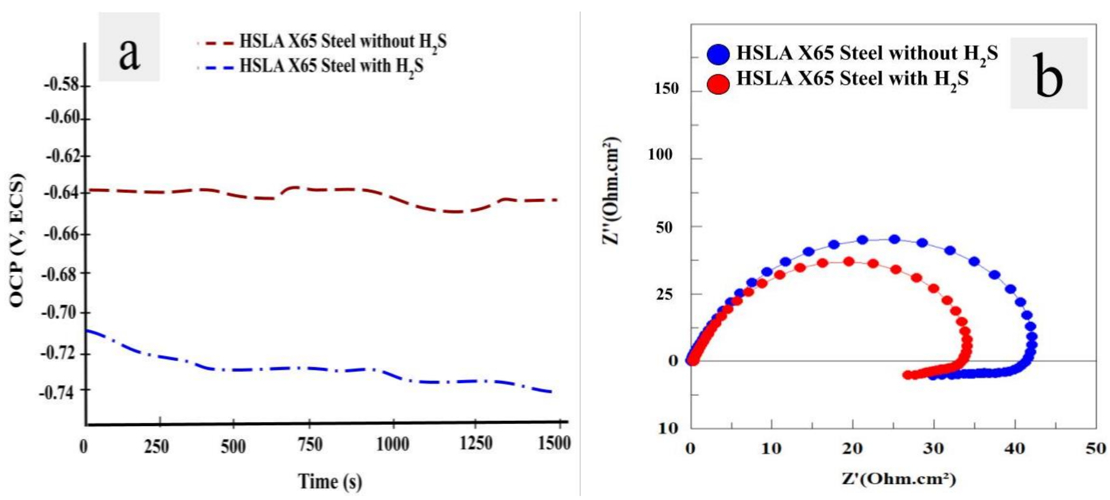

Figure 2. (a)Open Potential Circuit -OCP results and (b) Nyquist diagrams of HSLA X65 steel in solution A, NACE TM0284 (2016), without and with H_2S saturation.

Figure 3 presents the surface characterization of the samples exposed to the environment in the presence of H_2S that were the most corroded, whose surface by OM (Figure 3(a)) shows a generalized and localized attack in some regions, seen by SEM (Figure 3(b)) there is a localized attack, showing that the regions in the inclusions are regions with greater activity since in these regions the attack is more acute, whose EDS (Figure 3(c)) analysis shows producers rich in S, Mn, Fe that would correspond to the formation of sulfates and the dissolution of iron.

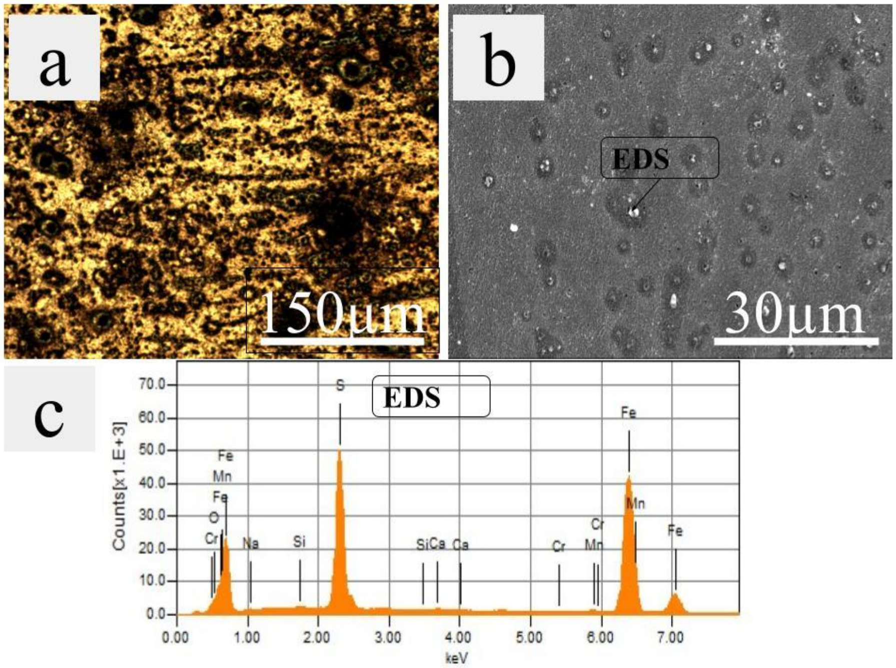

Figure 3. OM (a) and SEM (b) EDS analysis of HSLA X65 samples the electrochemical test. Exposure to solution A saturated with H_2S.

4. DISCUSSION

1. Analysis of inclusions and Microstructure analysis

The role of inclusions is very important to guarantee resistance to corrosion or resistance to embrittlement, irregular inclusions with a high concentration of MnS are considered deleterious and facilitate localized corrosion. (12-14) In this case, the HSLA X65 steel presents inclusions of a leased format with elements rich in Ca, Al, Ti which favor the formation of round inclusions and reduce MnS inclusions. On the other hand, the microstructure guarantees the mechanical properties, very hard phases in a steel can make it brittle, or very soft phases reduce the tensile strength. (13-14) The presence of perlite is associated with the percentage of carbon, cooling rate during the manufacturing process. For this HSLA X65 steel, the microstructure and grain size are as expected.

2. Electrochemical tests:

The electrochemical behavior is very important to complement the knowledge of a material against aggressive environments such as a sour gas environment. Gravimetric techniques take time and need several test bodies and more time to carry out; on the other hand, electrochemical impedance techniques such as EIS allow knowing the resistance to corrosion with greater ease of use and less time. (15-16) Likewise, environments rich in H_2S reduce the pH of the medium, facilitating corrosion, so the results are within those expected, the presence of hydrogen inside the material can directly affect the properties of the material, weaken the material so that the Structures used in the natural oil and gas industry must be practical, low-cost, and reproducible to complement quality control systems before certifying materials applied to this type of industry. (15-16)

5. CONCLUSIONS

In this investigation the following conclusions can be drawn:

1. Electrochemical tests proved to be a very useful tool for determining the electrochemical behavior, thus showing a reduction in the impedance modulus in the presence of H_2S, showing greater susceptibility to corrosion.

2. In sour gas media there is the formation of iron sulfate as a product of dissociation.

3. Inclusions of MnS can facilitate localized corrosion in sour gas media.

Conflicts of Interest: The authors declare that they have no conflicts of interest.

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CONFLICT OF INTEREST

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