# Influence of Exposure Time on Morphological and Electrochemical Properties of Corrosion Products Formed by High Temperature Sulfidation of AISI/SAE-1020 Steel

Javier A. Sanabria-Cala[a,*], Gerson R. Conde-Rodríguez[a], Dionisio A. Laverde-Cataño[a], Dario Y. Peña-Ballesteros[a], Hugo A. Estupiñan Durán[b]

[a]Grupo de investigaciones en corrosión, Universidad Industrial de Santander, Bucaramanga, Colombia. Parque Tecnológico Guatiguara, Km 2 vía refugio, Piedecuesta, A.A. 681011, Colombia
[b]Laboratorio de Biomateriales, Universidad Nacional de Colombia, Sede Medellín. Calle 75 # 79a - 51, Medellín, Colombia
 sanabriacalaj@gmail.com

In the present investigation, the influence of exposure time on the morphological and electrochemical properties of corrosion products formed on the surface of AISI/SAE-1020 steel was determined, exposed to conditions of a transfer line that enters the atmospheric distillation unit in the opportunity crude oils processing, applying gravimetry and electrochemical measurements. The exposure times used for gravimetric tests were between 24 and 330 hours. Discontinuous gravimetric tests were carried out in a Parr 4848 dynamic autoclave using a heavy crude oil (HCO) with sulfur content of 2.55 %wt. These results contribute to national and international scientific research and petrochemical industry by using a heavy crude oil contaminant such as sulfur, to reduce the corrosion rate of an AISI/SAE-1020 steel from the formation of iron sulfides on its surface.

## 1. Introduction

Corrosion is one of the main problems that affect global economy due to the large investment made by different industries in the equipment maintenance and repair. In petrochemical sector, corrosion generates a third of the faults that occur in different processes such as: exploration, drilling, production, refining and storage, greatly affecting the viability and durability of different equipment and transfer lines (Sanabria et al, 2017b). Due to their outstanding physicochemical properties, there is currently a reduction in light crude oils reserves, and heavy crude oils have become an alternative to supply world demand despite the technological challenge that represents their processing, due to the corrosion caused by pollutants contained in these crude oils from reservoirs (Jin and Nesic, 2017). Sulfur is found within this group of pollutants, and it is a corrosive agent that causes great economic losses to petrochemical industry due to sulfidation phenomenon, which is one of the corrosion types that occurs most frequently in this industry and is generated due to hydrogen sulfide ($H_2S$) produced during the thermal decomposition of a large variety of organic sulfur compounds (Sharifi et al, 2017). The influence of $H_2S$ on the materials corrosion rate by sulfidation can increase or decrease according to operating parameters such as: exposure time, temperature, alloy, pressure and fluid velocity (Rebak, 2011). However, sulfidic corrosion leads to the formation of layers of different iron sulfide compounds (FeS) as corrosion products, such as: mackinawite, troilite, pyrrhotite and pyrite; which can provide a certain protection degree to the material surface avoiding the attack of other corrosive species present in the environment (Jin et al, 2015). For this reason, experimental tests were developed in an environment that simulates a transfer line of heavy crude oil with high sulfur content, performing the study of morphological properties of the different corrosion products formed on the surface of AISI/SAE-1020 steel as a function of exposure time as operational parameter. Additionally, the corrosion rate generated by material sulfidation was calculated and the resulting corrosion products were analyzed by characterization techniques such as: Scanning Electron Microscopy (SEM) combined with Energy-Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD). Finally, the electrochemical properties of the formed corrosion products on the AISI/SAE-1020 steel were characterized by applying Electrochemical Impedance Spectroscopy (EIS).

## 2. Methodology

The AISI/SAE-1020 steel gravimetric coupons were machined to rectangular shape with dimensions of: 76.2 mm length; 12.5 mm width; and 1.5 mm thickness. Later, metallographic preparation was carried out according to ASTM G1-03 standard, uniformly polishing the six facets of each gravimetric coupon using silicon carbide sandpaper with numbers from 150 to 2000. Immediately, the coupons were cleaned in an ultrasonic bath with acetone and weighed on an XB220A reference analytical balance with ± 0.0001 g accuracy. The material chemical composition was determined by Spark Atomic Emission Spectrometry according to ASTM E415–17 Standard, obtaining 0.21 %wt carbon and 98.91 %wt iron as main components. Gravimetric tests were carried out in a dynamic batch autoclave at temperature of 350 °C and stirring speed of 100 rpm. A constant flow of high purity analytical nitrogen was supplied to the autoclave for 1 hour prior to the tests to eliminate the crude oil dissolved oxygen. The exposure times evaluated were 24, 36, 48, 60, 90, 120, 150, 180, 210, 250, 290 and 330 hours. During each gravimetric test, 6 gravimetric coupons were immersed in 1500 mL of a heavy crude oil (HCO) with total sulfur content of 2.5 %wt, API gravity of 12.2 ° and density of 0.98 g/mL at 15 °C. The corrosion rate of the AISI/SAE-1020 steel was calculated according to ASTM G1-03 standard. The electrochemical characterization of the FeS corrosion products was carried out at room temperature and atmospheric pressure in a three-electrode flat cell connected to a Gamry 3000 potentiostat/galvanostat, using an Ag/AgCl electrode (KCl 3M) as reference electrode; a graphite bar as counter electrode; and AISI/SAE-1020 steel as working electrode, with an exposed area equivalent to 1 cm$^2$. The electrolyte used for the electrochemical tests was a 3 %v/v NaCl solution. The EIS measurements were made applying 10 mV$_{rms}$, performing a frequency sweep from 100000 to 0.01 Hz recording 10 points per decade, in accordance with ASTM G3-89 standard. All electrochemical measurements were performed from the open circuit potential (OCP) recorded during 1 hour at the start of each test. The electrochemical characterization was carried out to determine the electrochemical properties of the FeS corrosion products formed on AISI/SAE-1020 steel, such as solution resistance ($R_\Omega$) and charge transfer resistance ($R_{ct}$).

## 3. Results and discussion

In Figure 1, the corrosion rate of AISI/SAE-1020 steel exposed to the processing of a heavy crude oil at constant temperature of 350 °C is shown. It was determined that corrosion rate of AISI/SAE-1020 steel does not show a linear increasing behavior with respect to all exposure times evaluated in the system. The corrosion rate of gravimetric coupons presented a linear increase up to 60 hours of exposure time, because during this interval the $H_2S$ formed in the system reacts with the exposed surface of the AISI/SAE-1020 steel, inducing the sulfidic corrosion of the material (Sanabria et al, 2017a). On the other hand, for higher exposure times such as: 90, 150 and 210 hours, a decrease in the corrosion rate of AISI/SAE-1020 steel was observed. This decreasing behavior is attributed to the FeS corrosion products formed on the AISI/SAE-1020 steel surface. The formation of FeS corrosion products starts with the thermal decomposition of organic sulfur compounds present in high concentrations in the heavy crude oil, obtaining as a main product hydrogen sulfide, which forms different layers of FeS by reacting chemically with the metal matrix (Lepore, 2016). According to obtained results, the formation of FeS layers with high stability and homogeneity on the material surface generated a reduction in steel corrosion rate up to 86 %, comparing the values obtained for 60 and 210 hours of exposition. However, at exposure times larger than 210 and up to 330 hours, a significant increase in the corrosion rate of AISI/SAE-1020 steel was obtained, reaching a value of 17.35 mpy. This corrosion rate behavior is caused by the formation of FeS layers on the material surface with low stability and homogeneity, that detach from the material and generate specific areas where a galvanic couple is formed and accelerate the deterioration of AISI/SAE-1020 steel in the system (Tang et al, 2010).
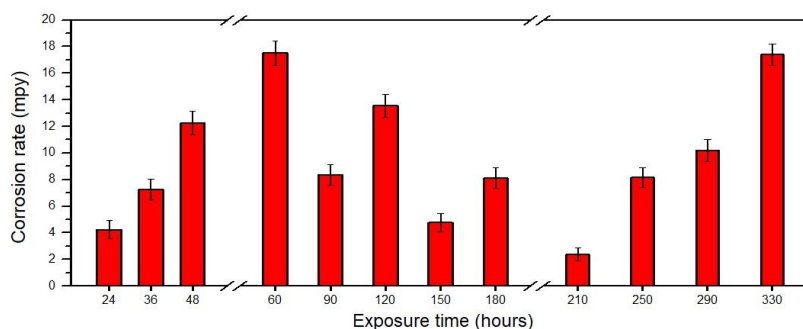


Figure 1: Corrosion rate of AISI/SAE-1020 steel exposed to heavy crude oil at 350 °C.

The morphology of FeS corrosion products formed on the AISI/SAE-1020 steel surface at temperature of 350 °C and exposure times of 90, 120, 150, 210 and 330 hours was studied by surface characterization technique SEM-EDS, as detailed in the micrographs of Figure 2. These conditions were selected based on the gravimetric analysis results, where it was shown that there is a significant reduction of AISI/SAE-1020 steel corrosion rate at those exposure times. In micrographs 2A is evidenced the formation of a layer composed mainly of marcasite type (FeS$_2$) iron sulfide, which is formed by grains with a size range between 1.722 to 1.985 µm, reaching an approximate sulfur content of 29 %wt on the surface and forming a crystalline structure with spinel morphology (Bai et al, 2014). In micrographs 2B are shown the corrosion products formed on the AISI/SAE-1020 steel exposed for 120 hours to a heavy crude oil, where it's possible to observe the formation on the steel surface of a non-homogeneous FeS bilayer which has fissures and is thermodynamically unstable; this is the reason the corrosion rate increased to approximately 13.5 mpy. At exposure time of 150 hours, the micrographs 2C show the evolution of the corrosion products to a homogeneous and stable layer composed mostly of pyrrhotite type (Fe$_{0.91}$S) iron sulfide. In addition, the grain size is increased, obtaining values between 1.307 and 2.229 µm, and sulfur content in the metal matrix reaches a value of 32 %wt, which is why there is a decrease in the AISI/SAE-1020 steel corrosion rate at those conditions (Rickard and Luther, 2007). At exposure time of 210 hours it is possible to affirm that the crystallinity degree of corrosion products increased, as seen in the micrographs 2D, since these are mainly composed of troilite (FeS) grains whose crystalline structure evolved to a stacked regular hexagonal type, with grain sizes from 1.446 to 4.289 µm and with sulfur content of 19 %wt (William, 2015). This type of stacked regular hexagonal structure presents a high thermodynamic stability due to its greater atomic packing factor, favoring the material protection as evidenced in Figure 1, where at 210 hours the lowest corrosion rate of the AISI/SAE-1020 steel was obtained, equivalent to 2.4 mpy (Rickard and Luther, 2007). At exposure times greater than 210 and up to 330 hours, there is a continuous increasing behavior of the corrosion rate of AISI/SAE-1020 steel, increasing the thickness of the FeS corrosion products formed on the steel surface. These corrosion products formed have a high degree of brittleness caused by the iron ions exit from the metal matrix towards the medium to react with hydrogen sulfide (Sun and Nesic, 2009). Due to this brittleness, the FeS layers already formed on the material surface are broken and detached, generating cycles of growth and detachment that are repeated periodically and contribute to the greater deterioration of the exposed metal surface in the system. Thus, when the surface of the material is exposed again to the corrosive medium, as illustrated in the micrographs 2E, zones are created that induce the formation of galvanic couples composed of two regions that are in simultaneous contact with the heavy crude oil, which acts as an electrolyte (William, 2015). The first region is anodic and corresponds to the exposed metal surface after the corrosion products detachment. The exposed surface has a decrease in its iron content from 98.91 (Table 1) to 81.08 %wt due to the diffusion and reaction of this element to form FeS layers, which are detached from the metal surface carrying a fraction of the iron initially contained in the steel. On the other hand, the second region is cathodic and corresponds to the FeS corrosion products generated by the sulfidation of AISI/SAE-1020 steel, which have a sulfur content of approximately 27 %wt. The formation of this galvanic couple generates an increase in the electrons transport through the system, which accelerates the dissociation of iron and favors sulfidic corrosion and other corrosive phenomena caused by different contaminating species that are present in the heavy crude oil (Tang et al, 2010).
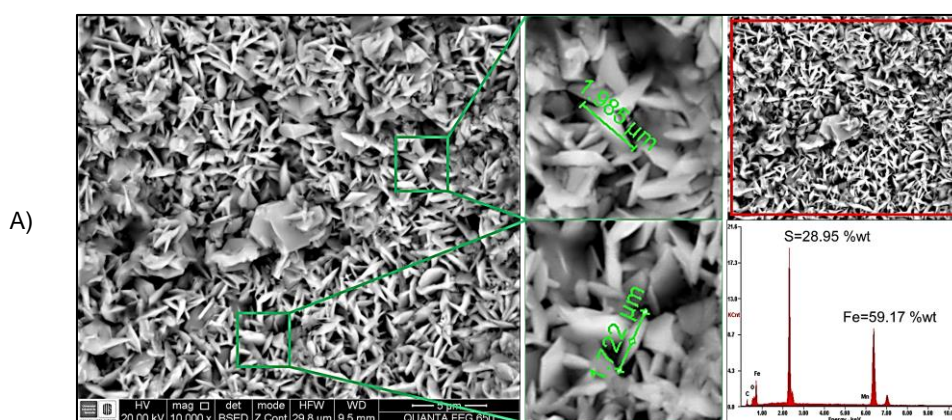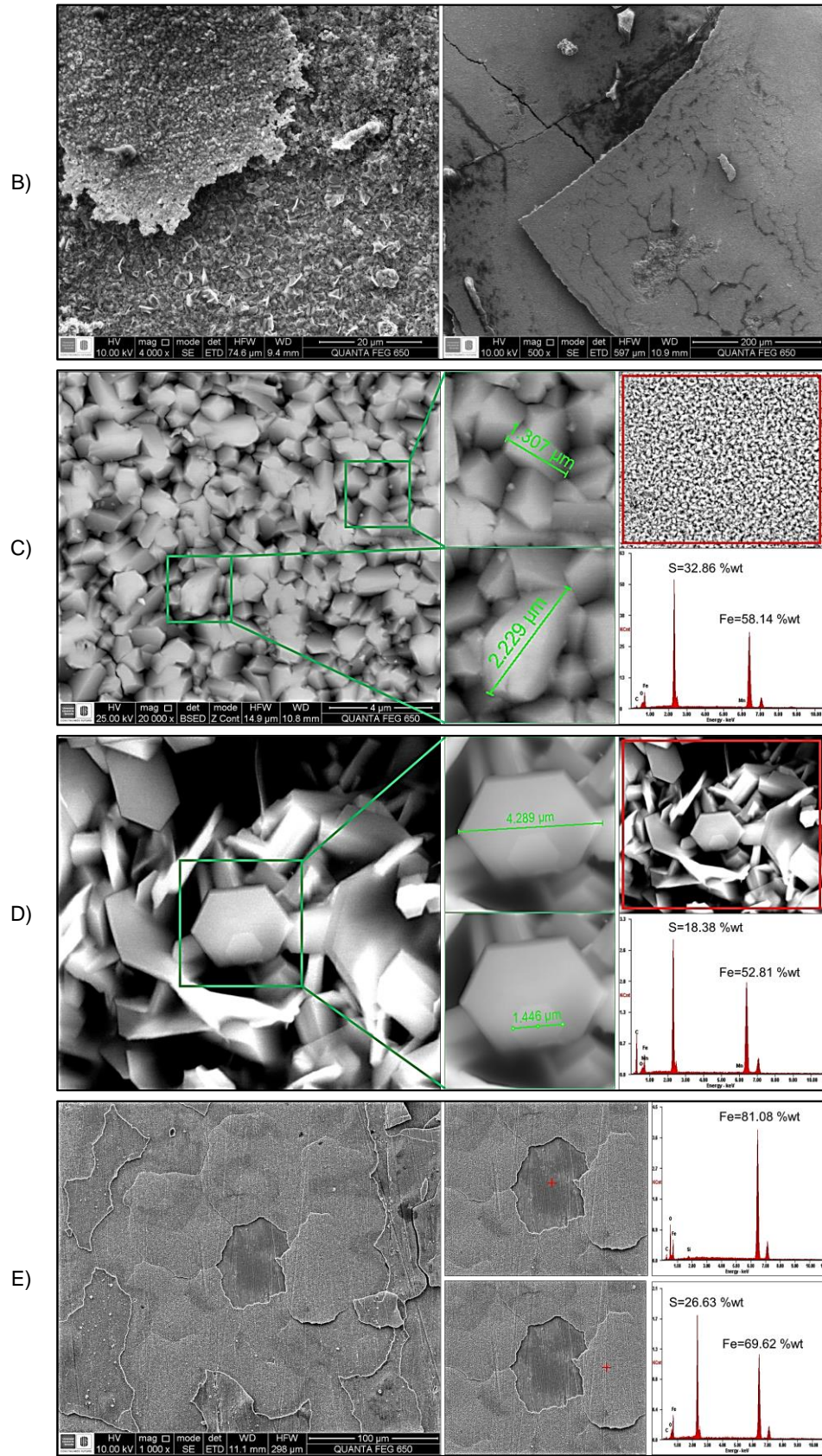


*Figure 2: SEM-EDS micrographs of corrosion products formed on AISI/SAE-1020 steel in HCO at 350°C after exposure times of A) 90 h, B) 120 h, C) 150 h, D) 210 and E) 330 h.*

*Figure 2 (continue): SEM-EDS micrographs of corrosion products formed on AISI/SAE-1020 steel in HCO at 350°C after exposure times of A) 90 h, B) 120 h, C) 150 h, D) 210 and E) 330 h.*

Prior to the electrochemical characterization of FeS corrosion products formed on the AISI/SAE-1020 steel surface, Open Circuit Potential measurements (OCP) were carried out for 1 hour to determine the anodic or cathodic tendency of the system, reaching a stable state. For all OCP tests, approximate values of 100 mV were obtained with oscillation amplitudes less than ± 5 mV. Next, the EIS tests were carried out, obtaining the Nyquist diagrams which were analyzed to determine the solution resistance and the charge transfer resistance of the corrosion products previously formed by the sulfidation of the steel AISI/SAE-1020, which are shown in Figure 3. The solution resistance values were determined at room temperature for all exposure times, obtaining an approximate average value of 1.25 ohms as related in Figure 3A. Due to the above, it is evident that the methodology used in the NaCl electrolyte preparation guaranteed the reproducibility of electrochemical measurements. As shown in Figure 3B, the charge transfer resistance of the FeS corrosion products formed at exposure times of 24, 36, 48, 60, 120, 180, 250, 290 and 330 hours has a decreasing behavior compared to the result obtained for the AISI/SAE-1020 steel metallic matrix. This behavior is due to the formation of non-homogeneous FeS corrosion products with low thermodynamic stability, which accelerate the charge transfer through the system because they do not generate a physical barrier that isolates the metal matrix from the electrolyte (Bai et al, 2015). On the other hand, for the FeS corrosion products formed at exposure times of 90 and 150 hours, the charge transfer resistance increases compared to the result obtained for the immediately previous time. This behavior is caused by the evolution of FeS corrosion products to more homogeneous structures on the AISI/SAE-1020 steel surface, which reduces the charge transfer through the physical barrier formed by these corrosion products (Huang et al, 2017). Finally, the FeS corrosion products formed at 210 hours of exposure to heavy crude oil have a homogeneous structure of stacked regular hexagonal type with high thermodynamic stability, which decreases the exchange of species between the electrolyte and AISI/SAE-1020 steel, allowing the system to achieve charge transfer resistance values greater than those obtained for the metal matrix (Bai et al, 2015).
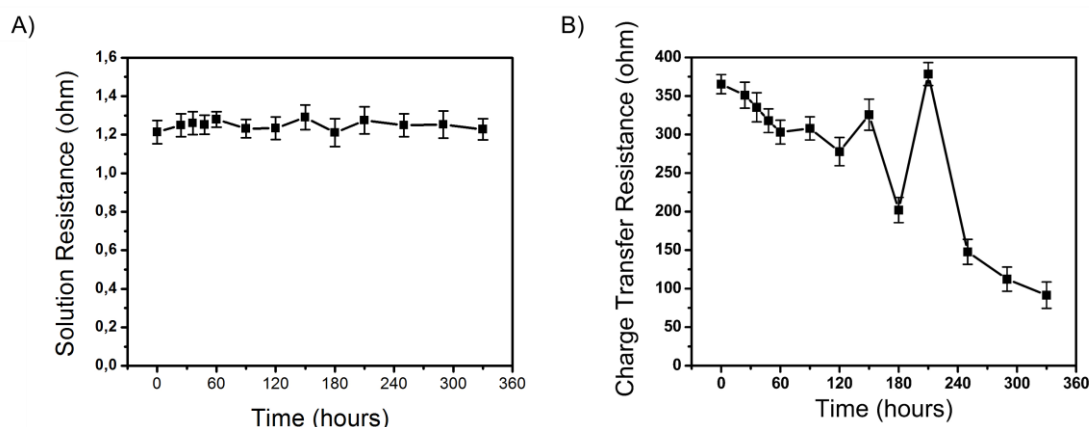


*Figure 3: Electrochemical Properties of FeS corrosion products.*

The analysis of the corrosion products formed at the AISI/SAE-1020 steel surface exposed to temperature of 350 °C for 90, 150 and 210 hours by XRD confirmed that the crystalline phases that are present with greater intensity correspond to iron sulfides. The determined crystalline phases and the charge transfer resistance obtained by EIS are listed in Table 2.

*Table 2: Sulfur-Compounds determined on AISI/SAE-1020 Steel exposed to HCO at 350°C.*

| Time [hours] | Charge Transfer Resistance [ohms] | Crystalline Phases | | |
|---|---|---|---|---|
| 0 | 365.36 | Iron (Fe) | | |
| 90 | 307.92 | Marcasite ($FeS_2$) | Troilite ($Fe_{0.985}S$) | Pyrrhotite ($Fe_{0.91}S$) |
| 150 | 325.70 | Pyrrhotite ($Fe_{0.91}S$) | Troilite ($Fe_{0.985}S$) | |
| 210 | 378.46 | Troilite (FeS) | Pyrrhotite ($Fe_{0.956}S$) | Pyrrhotite ($Fe_{1-x}S$) |

## 4. Conclusions

The study of high temperature sulfidation of AISI/SAE-1020 steel allowed to establish that the material corrosion rate does not increase linearly throughout the range of exposure times analyzed, because in the range between 60 to 330 hours, three cycles of growth and detachment of the FeS corrosion products of FeS formed on the surface of the material were noticed. For its part, the corrosion rate of AISI/SAE-1020 steel reaches its lowest value at an exposure time of 210 hours and 350 °C, evidenced by a reduction of up to 86 % during the three cycles. These cycles are caused by the formation of homogeneous corrosion products composed mainly of Troilite (FeS) with a stacked regular hexagonal structure. When formed as a corrosion product, the Troilite provides the material with a protection degree against other corrosive agents. Therefore, it is possible to affirm that the exposure of the AISI/SAE-1020 steel for 210 hours to a heavy crude oil corresponds to an optimum time for the formation of FeS corrosion products with better morphological properties. Finally, the charge transfer resistance of the FeS corrosion products is an electrochemical property strongly related to the crystalline phase, therefore, it could be used as a prediction tool for the crystalline structure of the corrosion products formed by the sulfidation of the AISI/SAE-1020 steel.

## Acknowledgments

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