Evaluation of corrosion products formed by sulfidation as inhibitors of the naphthenic corrosion of AISI-316 steel

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Abstract. Naphthenic acids present in oil from most regions worldwide currently stand as the main responsible for the naphthenic corrosion problems, affecting the oil-refining industry. The phenomenon of sulfidation, accompanying corrosion processes brought about by naphthenic acids in high-temperature refining plant applications, takes place when the combination of sulfidic acid (H₂S) with Fe forms layers of iron sulphide (FeS) on the material surface, layers with the potential to protect the material from attack by other corrosive species like naphthenic acids. This work assessed corrosion products formed by sulfidation as inhibitors of naphthenic corrosion rate in AISI-316 steel exposed to processing conditions of simulated crude oil in a dynamic autoclave. Calculation of the sulfidation and naphthenic corrosion rates were determined by gravimetry. The surfaces of the AISI-316 gravimetric coupons exposed to acid systems; were characterized morphologically by X-Ray Diffraction (XRD) and X-ray Fluorescence by Energy Dispersive Spectroscopy (EDS) combined with Scanning Electron Microscopy (SEM). One of the results obtained was the determination of an inhibiting effect of corrosion products at 250 and 300°C, where lower corrosion rate levels were detected. For the temperature of 350°C, naphthenic corrosion rates increased due to deposition of naphthenic acids on the areas where corrosion products formed by sulfidation have lower homogeneity and stability on the surface, thus accelerating the destruction of AISI-316 steel. The above provides an initial contribution to oil industry in search of new alternatives to corrosion control by the attack of naphthenic acids, from the formation of FeS layers on exposed materials in the processing of heavy crude oils with high sulphur content.

1. Introduction
Currently the world reserves of light crude oil have decreased significantly because their low concentrations of sulphur and naphthenic acids facilitate their refining, transport and storage, positioning them as the first choice of oil industry to supply the growing energy demand in national and international market. At this time, new alternatives are being explored for the processing of heavy crude oil that will position them as a strategic energy resource, which contribute to generate economic growth for the country and to sustain the current demand of fuels and other petroleum products in Colombia [1-3]. Heavy crude oils possess physicochemical characteristics such as: 1) high viscosity, 2) low API gravity and 3) high sulphur content, heavy metals and naphthenic acids. These characteristics condition the refining processes due to the great deterioration caused on the materials exposed to naphthenic corrosion and sulfidation, whence the processing of heavy crude oil is currently becoming an industrial challenge for the petrochemical sector [4].
The damages caused by naphthenic corrosion and sulfidation in the alloys of primary distillation units and their transfer lines is aggravated by the high pressure and temperature conditions that they are constantly subjected. In the refining of heavy crude oil with high sulphur content >2% w/w, it becomes a highly corrosive agent for materials exposed to temperatures >200°C [5]. Under these conditions, the thermal breakdown of sulphur generates the formation of H₂S, which is directly responsible for the sulfidation phenomenon. According to several investigations, the sulfidation of alloys leads to the formation of FeS as corrosion products on the material surface, among which is possible to find: 1) pyrite, 2) troilite and 3) mackinawite [5-6]. These products can reduce the corrosion rate caused by the attack of other corrosive species in the system, such as naphthenic acids, because they are formed on the surface and act as a physical barrier protecting the material [7]. Likewise, minimal changes in temperature and exposure time of petrochemical processes can lead to different results in the morphology of the formed FeS layers, and consequently increase the corrosion rate due to the formation of a galvanic couple on the exposed steel surface [7-8].

The formation of homogeneous and thermodynamically stable FeS layers depends on variables such as: 1) sulphur concentration in the heavy crude oil, 2) temperature, 3) fluid velocity and 4) exposure time of the material [2]. Therefore, in this study, the influences of temperature and exposure time on the formation of stable corrosion products from the sulfidation of AISI-316 steel were determined, exposed to the processing of a heavy crude oil with high sulphur content. Moreover, the anti-corrosive capacity of formed corrosion products was evaluated as a possible inhibitor of the naphthenic corrosion rate of AISI-316 steel, exposed to refining conditions of synthetic crude with a total acid number (TAN) equivalent to 1 mg KOH/g of crude oil. The gravimetric and microscopic results determined an inhibitory effect of the AISI-316 steel naphthenic corrosion rate, at temperatures between 250 and 300°C and exposure times of 144 and 192 hours, due to an iron sulphide layer formed as a corrosion product, whereby the naphthenic corrosion rates of the material presented a decreasing behaviour at these conditions in the system [9]. The above provides an initial contribution in the constant search of new alternatives directed towards the control of corrosion by the attack from naphthenic acids in oil industry, using a pollutant such as sulphur, present in high concentrations in the Colombian heavy crude oil.

2. Experimental
The coupons used for gravimetric tests were machined from AISI-316 steel, obtaining a rectangular shape with dimensions of: 37mm long, 12mm high and 2mm wide. The surface of the gravimetric coupons was prepared metallographically using sandpaper, initially of silicon carbide No. 400 until reaching a cloth of 0.05μm. To carry out the gravimetric tests, a type Parr model 4848 batch dynamic autoclave was used. All tests were performed in triplicate at a single stirring speed of 150rpm. The corrosion rate, in units of mpy (mils per year), was calculated according to the guidelines of ASTM Standard G1-03 (Standard practice for preparing, cleaning and evaluating corrosion test specimens) [10]. For the formation of corrosion products by the sulfidation of AISI-316 steel, tests are carried out at temperatures of 250, 300 and 350°C, and exposure times of 96, 144 and 192 hours.

During each test, the corresponding gravimetric coupons are placed in the reactor, and immersed in 1500mL of heavy crude oil with a sulphur weight percent of 2.5% w/w; API gravity of 12.2 and a density of 0.9848g/mL. A constant flow of high purity analytical nitrogen is supplied to the autoclave for one hour prior to the gravimetric tests in order to reduce the oxygen content dissolved in the crude. Once the sulfidation corrosion products are formed on the AISI-316 steel coupons surface, the inhibitory potential of naphthenic corrosion is evaluated by immersing the coupons with corrosion products in a solution of mineral oil and naphthenic acid with a TAN equivalent to 1 mg KOH/g crude oil; temperatures of 250, 300 and 350°C, and exposure times of 48, 96, 144 and 192 hours. After the tests are finished, the gravimetric coupons are cleaned for 1 hour with acetone in an ultrasonic bath and oven-dried at a temperature of 30°C for 5 minutes. Then, the coupons were weighed in an analytical balance with an accuracy of 0.0001g, labeled and stored in desiccator for gravimetric and superficial analysis. The corrosion products formed were characterized by: Scanning Electron Microscopy (SEM), in a device model Quanta Feg 650 equipped with System of Energy Dispersive of X-ray Spectroscopy (EDS); and
X-Day Diffraction (XRD), using a brand BRUKER model D8 DISCOVER diffractometer with DaVinci Geometry in beam mode.

3. Results and discussion
Preliminary studies have determined that at temperatures between 250 and 350°C and exposure times less than 96 hours, the H₂S present in the system exhibits a corrosive behaviour towards exposed AISI-316 steel. In addition, the SEM-EDS characterization did not evidence the formation of FeS layers on the material surface because the formation of FeS layers is governed by diffusion phenomena in solid state that depend on long exposure times, making each system unique [8]. Table 1 presents the corrosion rates by sulfidation of AISI-316 steel, where it is possible to observe that the corrosion rate increases as a function of temperature and exposure times. This behaviour is attributed to thermal breakdown of sulphur at high temperatures in hydrogen sulphide, which generates a difference of pressure in the system and favours its chemical reaction on the material surface, resulting in the formation by chemisorption of FeS-type corrosion products on the AISI-316 steel surface.

| Temperature (°C) | Corrosion Rate ± Standard Deviation (mpy) |
|-----------------|-------------------------------------------|
|                 | 96(h) | 144(h) | 192(h) |
| 250             | 0.0381±0.0002 | 0.0508±0.0003 | 0.0762±0.0003 |
| 300             | 0.0762±0.0003 | 0.0762±0.0002 | 0.0953±0.0002 |
| 350             | 0.1524±0.0001 | 0.1778±0.0002 | 0.2096±0.0003 |

The morphological analysis of the corrosion products formed on the AISI-316 steel surface was carried out using SEM. The selection of the coupons was made based on the results obtained from the gravimetric analysis; which indicated that at operating conditions of 350°C and an exposure time of 192 hours, the highest corrosion rate by sulfidation of AISI-316 steel was obtained. In the micrograph of Figure 1(A), the surface of the AISI-316 steel before being subjected to the sulfidation phenomenon is detailed. Furthermore, in the micrograph of Figure 1(B), is observed that the FeS grains formed on the surface of AISI-316 steel have a compact irregular crystal structure; finally, a homogeneous and stable layer whose grain size varies in a range from 396nm to 566nm is shown in the micrograph of Figure 1(C). On the other hand, the diffractograms shown in Figure 2 evince that the crystalline phase, present with greater intensity on the AISI-316 steel surface, exposed for 192 hours to a sulfidating atmosphere at 350°C of temperature, corresponds to an iron sulphide layer.

Figure 3 relates the naphthenic corrosion rates of AISI-316 steel exposed to the processing of a crude simulated with naphthenic acid of TAN=1 at temperatures of 250, 300 and 350°C, and exposure times of 48, 96, 144 and 192 hours. Figure 3(A) shows that the naphthenic corrosion rate of AISI-316 steel...
behaves in a linearly increasing manner due to the increase of all exposure times and temperatures in the system for coupons that do not have corrosion products formed by sulfidation on their surface. The highest deterioration of AISI-316 steel occurs at a temperature of 350°C and exposure time of 192 hours, reaching values of naphthenic corrosion rate of 1.7 mpy. This is because a higher temperature increases the reaction kinetics of naphthenic acids with the steel surface, resulting in higher corrosion rates in the material [7-9]. On the other hand, zone 1 of Figure 3(B) shows that the naphthenic corrosion rates of AISI-316 steel tend to stabilize at exposure times between 96 and 192 hours for temperatures of 250 and 300°C, which is due to the inhibitory effect generated by the iron sulphide layer formed on the material surface. On the contrary, zone 2 of Figure 3(B) shows that the naphthenic corrosion rates had a greater increase, and therefore, generated a great deterioration in the material compared to the corrosion rates of the coupons without iron sulphide on their surface, at a temperature of 350°C and times between 48 and 144 hours. This occurs due to the deposition of corrosive species, such as naphthenic acids, over areas where the iron sulphide layer is less stable, which causes their destruction and consequently an increase in the naphthenic localizes corrosion rate of the steel [6]. According to the obtained results, the iron sulphide layer formed by sulfidation on AISI-316 steel surface has influence on the naphthenic corrosion rates of the material, achieving values up to 20% lower than operating temperatures between 250 and 300°C and exposure times between 144 and 192 hours [8].

Figure 2. XRD of coupon surface at 192h and 350°C.

Figure 3. Corrosion rate of AISI-316 steel (A) Coupons without FeS and (B) With FeS.
The EDS analysis of the micrograph of Figure 4(A) is related in Table 2. There is a decrease from 9.97% to 6.77% in the sulphur content of the iron sulphide layer formed on AISI-316 steel surface after being exposed to naphthenic corrosion at a temperature of 300°C and an exposure time of 192 hours, conditions which the iron sulphide layer protects the material by reducing its naphthenic corrosion rate. Therefore, the EDS analysis of the micrograph of Figure 4(B), presented in Table 2, indicates that at exposure times of 192 hours and a temperature of 350°C, the sulphur content on the AISI-316 surface decreases from 9.97% to 4.78%, evidencing an aggressive attack to the iron sulphide layer by naphthenic acids. This damage in the iron sulphide layer favours the generation of a galvanic couple on the material surface, which can accelerate the deterioration of AISI-316 steel.

![Figure 4. SEM of AISI-316 steel coupon surface.](image)

**Table 2.** EDS of FeS layer exposed 192 hours to a simulated crude with TAN=1

| Element | Wt% (300°C) | Wt% (350°C) |
|---------|-------------|-------------|
| C       | 2.75        | 3.01        |
| Si      | 0.76        | 0.72        |
| Mo      | 2.33        | 2.13        |
| S       | 6.77        | 4.78        |
| Cr      | 15.70       | 16.05       |
| Ni      | 8.52        | 8.22        |
| Fe      | 55.24       | 49.24       |

**4. Conclusions**

The developed gravimetric tests determined the great influence of exposure time and temperature as fundamental variables in the formation of a stable and homogeneous corrosion product of iron sulphide on the AISI-316 steel surface, at the refining conditions of a heavy crude oil with high sulphur content. A reduction of the naphthenic corrosion rate of AISI-316 steel, exposed to a simulated crude with a TAN=1, was determined at temperatures between 250 and 300°C, and exposure times between 144 and 192 hours. This behaviour is due to the anti-corrosion effect generated by the formation of a homogeneous and compact layer of iron sulphide, as corrosion product of the steel sulfidation. Morphological analysis using surface-characterization techniques such as SEM-EDS showed the damage caused in the iron sulphide layer by the attack of naphthenic acids at a temperature of 350°C and an exposure time of 192 hours. The characterization by XRD allows determining the formation of an iron sulphide layer as a corrosion product, which acted as a physical barrier between the metal and the naphthenic acids, generating a protection towards the material; hence, it is possible to increase the useful life of the materials exposed to the processing of crude with high acidity content.
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