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Influence of Temperature and Time on the Corrosion by Sulfidation of AISI-316 Steel exposed under Transfer Line

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In this research, the influences of temperature and exposure time on the corrosion rate by sulfidation of an AISI-316 stainless steel were evaluated. It was exposed to different temperatures and times, simulating the transfer line entering to an atmospheric distillation unit in the crude oil processing. The gravimetric and surface characterization results indicated the strong influence of temperature and exposure time on evolution around a thermodynamically stable morphology. The iron sulfide layers (FeS) formed as corrosion products on the surface of AISI-316 steel, which played a protective role, reducing the material deterioration due to they acted as a barrier to the corrosion from other corrosive species in the system.

1. Introduction

One of the major oil and gas industry concerns is the understanding of corrosion phenomena induced by sulfur species impurities (Alvisi and Lin, 2011), (Suleiman, 2015). These are normally present within crudes and many times produced by hydrogen sulfide (H_2S), leading to a well know corrosion process by sulfidation (Mejia et al., 2015). The sulfidation process is generally an irreversible corrosion process in that the sulfur that is released during reoxidation of the sulfides can penetrate the substrate alloy along the grain boundaries, thereby affecting the mechanical integrity of structural components (Torres et al., 2016), increasing the corrosion rates on reactors and pipelines based on steel and its alloys (Heather et al., 2016). However, literature reports about metal morphological features of corrosion products formed by sulfidation phenomena are scanty, especially when the occurrence is associated with the surface layer of an austenitic stainless steel (Hucińska et al., 2006). During heavy crude oils processing is important to take into account the highly corrosive effects, produced by their high sulfur concentration (1-3%w/w) depending on the type of hydrocarbon (Serna, 2003). This characteristic of heavy crude oils composition and the high temperatures they are subjected in the refining processes, deteriorate the equipment generating incrustations and corrosive products in the different lines of the process, depending on its manufacturing material (Kapusta al., 2003). Corrosion by sulfidation at high temperatures (>232°C), (Serna, 2003), is generated by the thermal breakdown of sulfur to produce hydrogen sulfide (H_2S) (Qi et al., 2014), which under certain operating conditions is highly corrosive and degrades materials (Sanabria et al., 2014). However, under certain conditions of temperature, exposure time, pressure, alloy type, fluid velocity and sulfur concentration in the heavy crude oil (Zheng et al., 2015); it can provide some degree of protection to the material, forming FeS layers as corrosion products, for instance: 1) pyrite, 2) troilite and 3) mackinawite (Ning et al., 2014). Therefore, in this study, the influences of temperature and exposure time in the formation of FeS layers as corrosion products (Zheng et al., 2013), on the AISI-316 steel surface were evaluated exposed to the processing of a heavy crude oil with high sulfur concentration. The corrosion rate of the material was calculated and the corrosion products formed on the steel surface were characterized in order to obtain the present phases and their morphology. Results showed the generation of an iron sulfur layer that probably inhibited the corrosion caused by different pollutants and which provide protection to the material under certain operating conditions (Yameng et al., 2014). Also it can

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be observed in the corrosion rates, whose changes according to exposure time were compared. In this case, testing from 36 to 60 h, and observing a reduction of the corrosion rate from 0.0042 to 0.0022 mm/y at 330°C. The formed sulfur mineral was analyzed by X-Ray Diffraction (XRD), identifying a troilite (FeS) phase. With these results, is possible thinking about a potential reduction in the operating costs, which are normally increased by changing pieces of the process devices due to corrosion; according to this research, the corrosive attack can be controlled even by sulfidation corrosion (FeS formation), mitigating the material corrosion rate in the system (Yonn et al., 2010).

2. Methodology

Coupons for gravimetric tests were machined from AISI-316 steel, obtaining a rectangular shape with dimensions: 37 x 12 x 2 mm, which were characterized based on ASTM E-415 standard, using an optical emission spectrometer. The coupons faces were homogenized by the use of silicon carbide sandpaper, the treatment started with sandpaper Number 240 and following with Number 400, 600, 1000, 2000, 2400 to reach a cloth of 0,05 µm; this procedure was based on ASTM G1-03 standard. Subsequently, the coupons were cleaned with acetone in an ultrasonic bath and dried with hot air, in order to be used in the gravimetric measurements, which were carried out in a batch-type dynamic autoclave, where the AISI 316 steel coupons were immersed in 1000 mL of a heavy crude oil with a sulfur weight percentage of 2.5 % w/w. In all cases, the gravimetric tests were performed with a single stirring speed (100 rpm) and a constant flow of high purity analytical nitrogen was supplied to the autoclave for one hour prior to the tests, in order to reduce the content of dissolved oxygen in the crude. Each experimental condition was evaluated by a set of samples consisting in four gravimetric coupons. The gravimetric tests were carried out at different exposure times of 36, 48, and 60 hours at temperatures of 250, 290 and 330 °C, according to ASTM G1-03 Standard. The obtained corrosion rate is directly related to mass loss by the material exposure in the system. Once the tests were finished, the gravimetric coupons were degreased with acetone (this process was performed in an ultrasonic bath), they were weighed on an analytical balance with an accuracy of ± 0.0001 g, in order to be labeled and stored in a desiccator, for further gravimetric and superficial analysis. Subsequently, the exposed coupons were characterized by surface characterization techniques as: Scanning Electron Microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS), in a device model Quanta Feg 650 equipped with X-ray energy dispersion system (EDX), moreover, they were mounted and adjusted on a platform from the Eulerian cradle of the brand BRUKER equipment model D8 DISCOVER with DaVinci Geometry, where the measurement was performed by an X-ray diffractometer in beam mode, in order to identify and characterize the crystalline phases present on the material surface and infer the compounds that were formed and their relation with the behavior of the corrosion rate from AISI-316 steel in the system. Finally, for the study of the roughness and the topographic imaging at micrometric scale of the formed corrosion products, a VEECO di-CP II Atomic Force Microscope (AFM) was used operated in air, working in non-contact mode, using a silicon tip which scanned areas, each with dimensions of 10 x 10 µm in each of the samples.

3. Results and discussion

The corrosion rates of AISI-316 steel obtained from the performed gravimetric tests are listed in Table 1.

Table 1. Corrosion rates of AISI-316 steel [mm/y]

Temperature [°C]	36 [h]	48 [h]	60 [h]	standard deviation		
				36 [h]	48 [h]	60 [h]
250	0.0093	0.0077	0.0079	0.0002	0.0003	0.0003
290	0.0046	0.0040	0.0039	0.0003	0.0002	0.0002
330	0.0042	0.0032	0.0022	0.0001	0.0002	0.0003

These results show that for all temperatures and exposure times, the corrosion rate of AISI-316 steel gravimetric coupons has a non-linear decreasing behavior; this behavior is attributed to the products of the thermal breakdown of sulfur at high temperatures, mainly the H_2S (Houyi et al., 2010). This is explained by the solid state diffusion of the corrosive H_2S with the metal surface to form FeS layers through a corrosion mechanism by dissociation of H_2S on the metal surface (Yameng et al., 2012), which deposits a thin but strongly adhered film on this surface (Ramanarayanan and Smith, 1990). This FeS film reduces the corrosion rate because the reactive species are depleted on the metal surface (Smith and Joosten, 2006), while the corrosion products accumulate on the steel surface (Singer et al., 2012); therefore, a concentration gradient is established on both sides of the thin film (Ning et al., 2014).

Table 2. EDS zone 1 and 2 of coupon surface at 60 hours of exposure and 330 °C.

Element (zone 1)	Wt%	At%	Element (zone 2)	Wt%	At%	standard deviation
FeL	55.3	46.4	FeL	55.3	46.4	0.01
SK	32.6	33.7	SK	8.62	12.7	
CrK	17.3	15.6	CrK	17.3	16.6	

The surface morphology of the films formed on AISI-316 steel coupons was analyzed by SEM-EDS, based on the obtained results from the gravimetric analysis, where the lowest values of the material corrosion rates were selected, which were obtained at temperature conditions of 330°C and exposure times of 36, 48 and 60 hours respectively. The obtained micrographs from the formed films of FeS are shown, which show a uniformity in the surface without evidence of porosity, homogeneous, good adhesion and with an increase in the size of the agglomerates in a range that varies between 85 and 285 nm, in a longer immersion time and sulphur content on the surface of 5.4 %w/w to 8.7 %w/w, as shown in the Figure 1 (Pengpeng et al., 2014). The micrography in Figure 2 and EDS in Table 2, shows another layer grown on the already formed layer, which have their maximum increase in sulfur content on the surface of 32.6 % w/w in the zone 1 and 8.6 % w/w in the zone 2, hence, the formation of bilayers is guaranteed, which at greater immersion time evolve to a larger FeS film on the material surface, providing a greater protection in the material against the corrosive environment (Jun-Seob et al., 2016). The crystalline structures of the corrosion products formed on the steel surface were studied, the results determined that the only main homogeneous phase formed at 36, 48, and 60 hours of exposure and 330°C is troilite, as detailed in Figure 3.

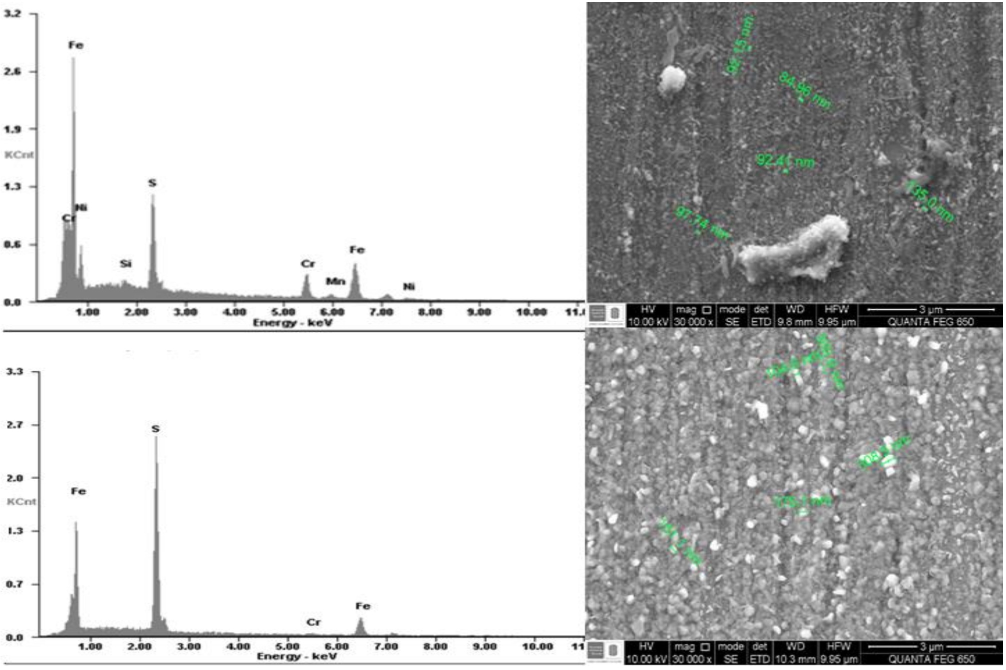

Figure 1. SEM-EDS of coupon surface at 36 and 48 hours of exposure and 330°C.

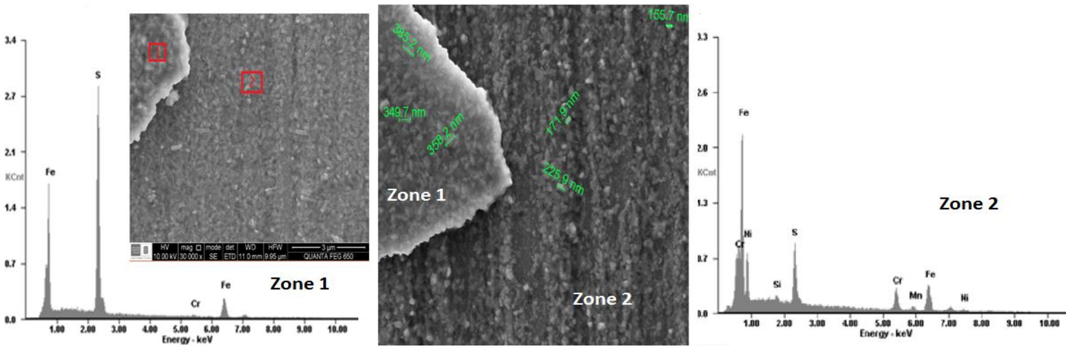

Figure 2. SEM-EDS of coupon surface at 60 hours of exposure and 330 °C

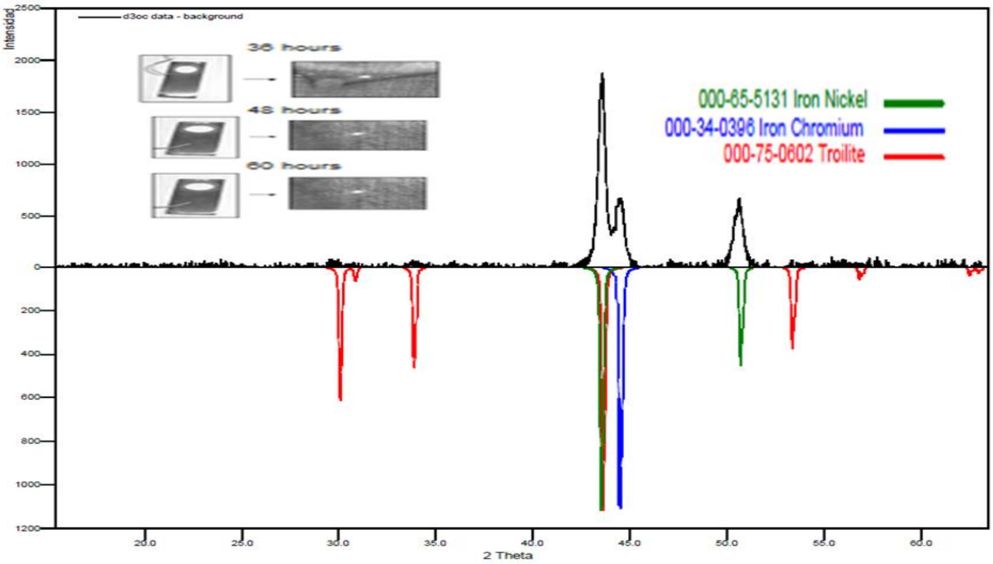

Figure 3. DRX of coupon surface at 36, 48 and 60 hours of exposure and 330°C.

Figure 4 shows the micrometric topographic images of AFM taken on the surface of gravimetric coupons exposed to different immersion times of 36, 48 and 60 hours and a temperature of 330°C. Table 3 shows the values obtained in the measurements of troilite film roughness (formed on the surface of the AISI-316 steel (Freitas et al., 2012), it also shows the decrease of the values of film roughness with the increase of immersion time at 330°C, this indicates that the corrosion rates of AISI-316 steel decrease considerably as the roughness of FeS film formed in the material decreases (Min et al., 2016), (Jun-Seob et al., 2016), therefore, obtaining a homogeneous layer of troilite on the steel surface reduces the possibility of corrosion by intrusion, a type of localized corrosion in which the protective layer formed of FeS is eliminated in specific areas, being exposed to the formation of a galvanic pair between the exposed metal and other present corrosive species that act as an electrolyte, which accelerates the process of material damage in the system, this is likely related to accelerated H_2S corrosion at pre-existing defects on the metal surface (Houyi et al., 2010).

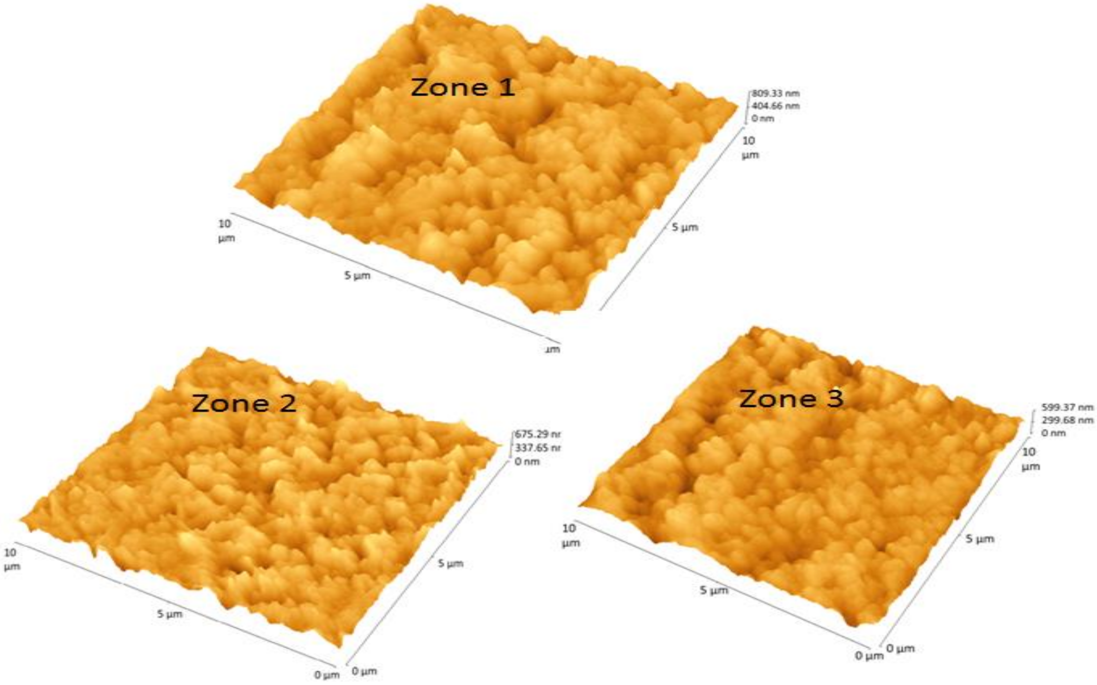

Figure 4. Topographical AFM images of coupon troilite at 36, 48 and 60 hours of exposure and 330°C

Tabla 3. Roughness values of troilite film.

Image	Roughness RMS (nm) Zone 1	Roughness RMS (nm) Zone 2	Roughness RMS (nm) Zone 3	standard deviation
36 hours	72.2	90.2	85.2	0.01
48 hours	58.5	50.5	68.5	
60 hours	45.1	40.1	39.1	

The figure 5, shows the cross sections and EDS of gravimetric coupons that were exposed to conditions of 330 °C, 36, 48 and 60 hours, it indicates the thickness from troilite films formed on AISI-316 stainless steel surface by microscopy, and highlights the importance of exposure time in increasing layer thickness where troilite film varies its thickness from 875 nm to 1.7 μm and sulfur percentage from 1.8 % w/w to 10.8 %w/w. Under analyzed operating conditions, it benefits the obtaining of a homogeneous and compact layer which mitigates the corrosion rate of AISI-316 steel (Min et al., 2016).

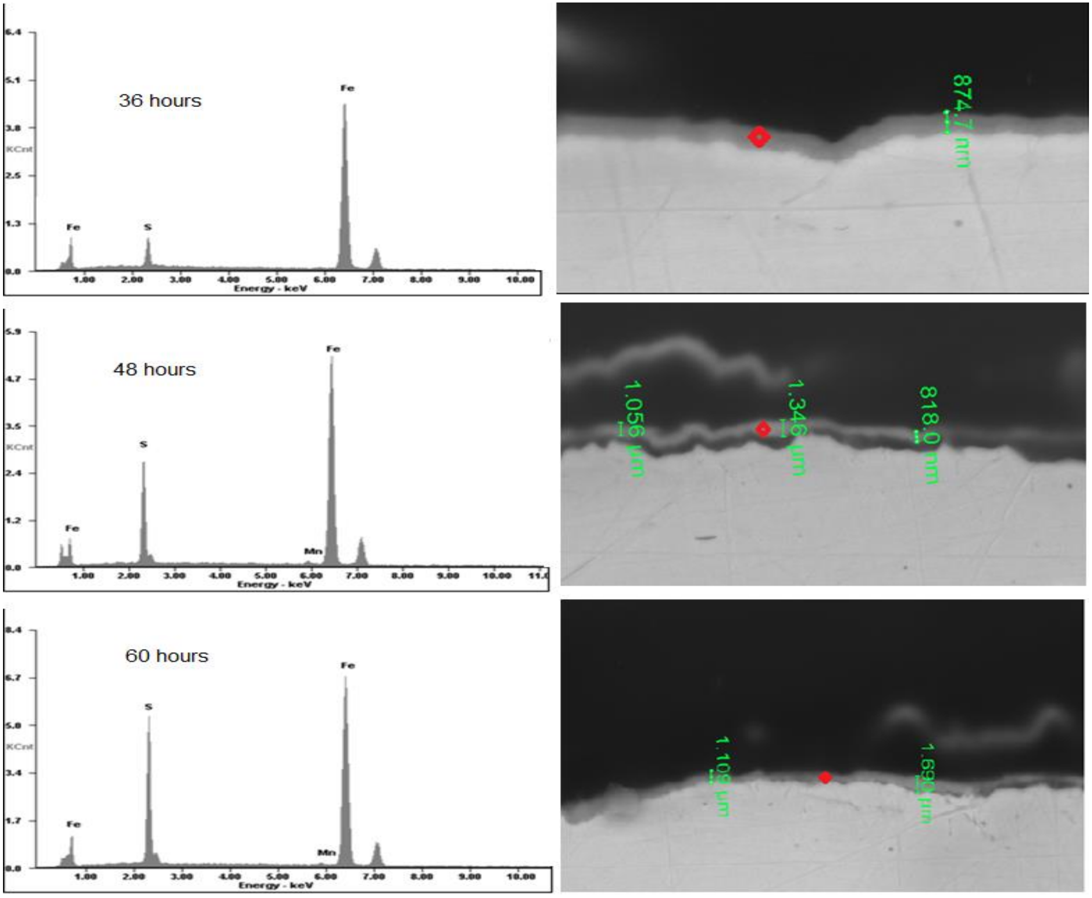

Figure 5. Troilite film thickness from coupon at 36, 48 and 60 hours of exposure to 330°C.

4. Conclusions

In summary, corrosion products via the reaction of iron and hydrogen sulfide in both vapor and liquid phases are identified. The nature, thickness, and morphological properties of FeS films which give a protective role to AISI-316 steel are controlled by temperature and exposure time. The protectiveness of the outer iron sulfide layer depends on the balance between iron sulfide precipitation which forms the layer and the corrosion which undermines it. According to the analysis of the gravimetric evaluation that was developed in the system simulating temperatures inherent to a transfer line in the processing of a heavy crude oil with high sulfur concentration, between 250 and 330°C and a range between 36 and 60 hours of exposure, showed a continuous decrease in the corrosion rate of AISI-316 steel, this is due to the formation of a thermodynamically stable film of troilite on the material surface. The results of the surface characterization by SEM-EDS, DRX and AFM showed that the homogeneity of the formed film increases with the exposure time and the temperature, furthermore, they allowed to determine that the corrosion product formed on the surface of AISI-316 steel with increasing exposure time and temperature acquires an irregular morphology without defined crystal structure. These observations have aroused the interest of studying the physicochemical nature of the corrosion products adhered to AISI-316 steel in order to know its passivating properties and their effect on the steel corrosion.

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